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PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Docket No: Q76500

Yasuyuki HOSHINO, et al.

Appln. No.: 10/614,207

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For: FLUORINATION TREATMENT APPARATUS, PROCESS FOR PRODUCING
FLUORINATION TREATED SUBSTANCE, AND FLUORINATION TREATED
SUBSTANCE

SUBMISSION OF VERIFIED ENGLISH LANGUAGE TRANSLATIONS

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Applicants respectfully submits herewith for the above-identified application, three (3) verified English translations of the related provisional applications listed below with executed translator's Declaration for each provisional application previously filed in the Japanese language.

1. U.S. Provisional Application No. 60/397,610 filed July 23, 2002, with 32 pages of verified English language translation of specification, 5 pages of drawings, plus executed translator's Declaration.

2. U.S. Provisional Application No. 60/470,900 filed May 16, 2003, with 37 pages of verified English language translation of specification, 6 pages of drawings, plus executed translator's Declaration.

3. U.S. Provisional Application No. 60/473,890 filed May 29, 2003, with 27 pages of verified English language translation of specification, 6 pages of drawings, plus executed translator's Declaration.

SUBMISSION OF VERIFIED ENGLISH LANGUAGE TRANSLATIONS

U.S. Application No.: 10/614,207

Attorney Docket No.: Q76500

The Examiner is respectfully requested to acknowledge receipt of said verified translations.

Please charge any fee that may be necessary in connection with the filing of this paper to Deposit Account No. 19-4880. A duplicate copy of this paper is attached.

Respectfully submitted,



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Date: November 17, 2003



DECLARATION

I, Yayoi HONDA, c/o S.SUZUKI & ASSOCIATES, 13-6,
Nishigotanda 7-chome, Shinagawa-ku, Tokyo, Japan, do solemnly
and sincerely declare that I understand the Japanese language
and the English language well, and that the attached English
version is a full, true and faithful translation made by me
of the US Provisional Application No. 60/397,610 (July 23, 2002).

I make this solemn declaration conscientiously believing
the same to be true.

November 7, 2003

Yayoi Honda
Yayoi HONDA



[Name of Document] SPECIFICATION

[Title of the Invention]

FLUORINATION HEAT TREATMENT APPARATUS,

PROCESS FOR TREATING A SUBSTANCE AND TREATED SUBSTANCE

5 [Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a fluorination heat treatment apparatus for carrying out treatment of a substance
10 by forming a fluorine atmosphere free from impurity contamination, a process of treating a substance and a substance treated by the treating process.

[0002]

[Background of the Invention]

15 Fluoride materials are transparent even in a vacuum ultraviolet region where the wavelength is not more than 180 nm different from nitrides or oxides so that they are essential materials for optical elements used in the vacuum ultraviolet region such as lenses, prisms etc, and optical thin films coated
20 on the surfaces of these optical elements, such as anti-reflection coatings, deflection films or reflection films.

[0003]

The development of a reduced projection exposure
25 apparatus for producing semiconductor circuits in which vacuum

ultraviolet light is used as an exposure light source has been demanded in order to produce fine circuit patterns with photolithography in accordance with recent higher integration and higher densification of semiconductor integrated circuits.

5 For the reduced projection exposure apparatus for vacuum ultraviolet light, various fluoride optical elements and optical thin films are used.

[0004]

The reduced projection exposure apparatus is provided
10 with several tens of fluoride optical elements having various shapes and uses between a laser light source to a wafer in which a semiconductor circuit is exposed, and the surfaces of the optical elements are coated with a fluoride thin film suitable for the object. The optical element materials and the fluoride
15 thin films have more or less light absorption so that the quantity of light finally reached to the wafer surface becomes fairly small. In order to improve the exposure performance and productivity, it is necessary to diminish a decrease of the quantity of light. That is, light absorption of each optical
20 element and each thin film is decreased so that the properties of the exposure apparatus are improved.

[0005]

The optical element materials have been earnestly studied and developed for many years. As a result, the faults
25 and the impurity content causing light absorption are depressed

to the utmost and scattering on the element surface is lowered to the utmost by the development of polishing technique.

On the other hand, optical thin films are simply formed at a relatively lower temperature by various PVD methods such as vacuum deposition with resistive heating or electron beam dissolution, vacuum deposition in the combined use of ion assist, ion plating, sputtering or ion beam sputtering. The reason why the optical element used as a substrate is heated at a relatively lower temperature and a thin film is formed that if it is heated at a high temperature, the optical element is deformed with heat to induce error in processing dimension accuracy on the optical element surface with the result that the desired image formation performance can not be obtained.

[0006]

The fluoride optical thin film thus formed on the optical element with heating at a relatively lower temperature has a markedly higher light absorption as compared with a bulky fluoride solid formed at a high temperature for a long time. The thin film has a markedly larger vacuum ultraviolet light absorption toward the bulky fluoride solid with the following reasons that a fluorine loss is caused compared to the stoichiometric composition to induce dangling bond, a fluorine lacking atom site is linked with an oxygen atom or a hydroxyl group so as to absorb light, the thin film has low crystallizability and has many structural faults as compared

with the bulky fluoride solid, and it has a large specific surface area as compared with the bulky fluoride solid and thereby contains very large adsorption amounts of moisture or organic matters and these adsorbed matters absorb light.

5 [0007]

The optical thin films are applied on the both surfaces of an optical element so that the number of coated surfaces is twice the number of the optical elements. So, when optical thin films having a high light absorption are mounted on the vacuum ultraviolet light exposure apparatus accompanied with a fluorine loss, structural irregularity, oxidation and hydroxylation, and moisture and organic matter adsorption, the quantity of light which reaches to the wafer surface through the several tens coated optical thin films becomes very low, e.g. about several% of the original light quantity of the light source. Therefore, the exposing time is prolonged and the productivity becomes low extremely. That is, the exposure performance is determined by the optical thin film. Additionally, fluorine lacking fluoride thin films, or fluorine-lacking and oxygen-containing fluoride thin films have not so high leaser durability due to the structural faults and inclusion of impurities, so that optical element parts are frequently exchanged to further decrease the productivity of the exposure apparatus.

25 [0008]

The object of the invention is to provide a fluorination heat treatment apparatus capable of improving the transmittance in vacuum ultraviolet ray region by decreasing the fluorine loss of a substance, such as fluoride thin films, etc, a process for treating a substance such as fluoride thin films, etc and a substance treated with this process.

[0009]

[Means for solving the object]

The present inventors have earnestly studied and found that a fluorine gas has the highest reactivity among all the elements, and thereby chemical reaction is caused between various kinds of matters and fluorine gas in the fluorine gas feeding line or a substance treating apparatus, and the resulting substances produced from the chemical reaction may include substances which contaminate optical elements accommodated in a treating apparatus, so that the effect of improving the transmittance with the fluorination heat treatment cannot be maximally exerted. Thus, the present invention concerning to the fluorination heat treatment apparatus, the process for treating substances and the substances treated by the process has been accomplished.

[0010]

The fluorination heat treatment apparatus as defined in claim 1 comprises

a fluorine gas storage and feeding vessel for storing a

fluorine gas and feeding the fluorine gas,

a reactor for conducting fluorination heat treatment of
a substance and

a fluorine gas piping extending from the fluorine gas
5 storage and feeding vessel to the reactor, wherein at least
portions which come in contact with fluorine gas comprise a
material having a chromium concentration of not more than 1 %.
[0011]

The fluorination heat treatment apparatus as defined in
10 claim 2 comprises:

a fluorine gas storage and feeding vessel for storing a
fluorine gas and feeding the fluorine gas,

a reactor for conducting fluorination heat treatment of
a substance and

15 a fluorine gas piping provided from the fluorine gas
storage and feeding vessel to the reactor, wherein at least
portions which come in contact with the fluorine gas comprise
a material having a titanium concentration of not more than 1 %.
[0012]

20 The fluorination heat treatment apparatus as defined in
claim 3 is characterized in that the material comprises at least
one of nickel, a nickel alloy, copper, a copper alloy, aluminum
and an aluminum alloy.

[0013]

25 The fluorination heat treatment is carried out by the

fluorination heat treatment apparatus as defined any one of claims 1 to 3 so that not only the fluorine loss of the substance treated are compensated but also impurities are decreased, and the substance can be changed into a fluoride having a stoichiometric composition. Additionally, carrying out the fluorination heat treatment, the crystallinity of the substance can be improved and the structural faults thereof can be decreased. Further, carrying out the fluorination heat treatment, the leaser resistance of the substance can be also improved.

[0014]

The process of treating a substance as defined in claim 4 comprises:

a step of placing the substance into a reactor provided in a fluorine heat treatment apparatus as defined in any one of claims 1 to 3,

a pressure control step of controlling a total pressure and a fluorine partial pressure in the reactor provided in the fluorination heat treatment apparatus into predetermined pressures, and

a temperature control step of controlling the temperature in the reactor into a predetermined temperature.

The process of treating a substance as defined in claim 5 comprises:

a step of placing the substance into a reactor provided

in a fluorine heat treatment apparatus as defined in any one of claims 1 to 3,

a fluorination reaction step of subjecting the substance placed in the reactor to fluorination reaction, and

5 a heating step of heating the substance placed in the reactor to a predetermined temperature.

The process of treating a substance as defined in claim 6 comprises:

a step of placing the substance into a reactor provided
10 in a fluorine heat treatment apparatus as defined in any one of claims 1 to 3,

a moisture removing step of removing moisture in the reactor with deaeration,

a fluorination reaction step of subjecting the substance
15 placed in the reactor to fluorination reaction,

a cooling step of cooling the substance placed in the reactor, and

a taking out step of taking out the substance from the reactor

20 wherein in the moisture removing step, the treating temperature is from 100 to 170°C, and in the fluorination reaction step, the temperature in the reactor is from 10 to 150°C and the fluorine concentration is from 1000 ppm to 100%.

[0015]

25 The process of treating a substance as defined in claim

7 comprises:

a step of placing the substance into a reactor provided in a fluorination heat treatment apparatus as defined in any one of claims 1 to 3,

5 a moisture removing step of removing moisture in the reactor with deaeration,

a fluorination reaction step of subjecting the substance placed in the reactor to fluorination reaction,

10 a heat treating step of heating the substance placed in the reactor to a predetermined temperature,

a cooling step of cooling the substance placed in the reactor, and

a taking out step of taking out the substance from the reactor,

15 wherein in the fluorination reaction step, the temperature of the reactor is from 10 to 150°C and the fluorine concentration is from 1000 ppm to 100%, and further the temperature of the reactor in the heat treating step is higher than the temperature of the reactor in the fluorination
20 reaction step and the fluorine concentration in the reactor in the heat treating step is lower than the fluorine concentration of the reactor in the fluorination reaction step.

[0016]

The process of treating a substance as defined in claim
25 8 is characterized in that the substance comprises at least one

of a fluoride thin film, a fluoride powder, a fluoride solid and a fluoride optical element.

[0017]

The process of treating a substance as defined in claim 5 9 is characterized in that the fluoride thin film, fluoride powder, fluoride solid and fluoride optical element each comprise at least one selected from the group consisting of magnesium fluoride, calcium fluoride, lithium fluoride, lanthanum fluoride, aluminum fluoride, neodymium fluoride, 10 gadolinium fluoride, yttrium fluoride, dysprosium fluoride, barium fluoride, sodium fluoride, bismuth fluoride, strontium fluoride, lead fluoride, selenium fluoride, cryolite and chiolite.

[0018]

15 The process of treating a substance as defined in claim 10 is characterized in that the fluorine used comprises at least one of pure fluorine gas; a fluorine gas diluted with at least one rare gas of helium, neon, argon, krypton and xenon; a fluorine atom liberated from the inside of the reactor 20 fluorinated previously during the treatment; a fluorine atom liberated during the treatment from the reactor in which a previously fluorinated metal, a fluorine excess alloy or a fluorine excess fluoride is placed; a fluorine gas generated by electrolysis of a metal fluoride; a fluorine gas obtainable 25 by sublimating and evaporating a fluorine-rare gas compound

such as XeF_2 , XeF_4 or XeF_6 and by decomposition of these fluorine and rare gas compounds; and an active fluorine of a fluorine radical and a fluorine ion generated by dissociating at least one of a carbon-fluorine compound, sulfur-fluorine compound
5 and nitrogen-fluorine compound.

[0019]

According to the processes for treating a substance as defined in claims 4 to 10, not only the fluorine loss of the substance is compensated but also impurities are decreased, and
10 the substance can be changed into a fluoride having a stoichiometric composition. Additionally, the crystallinity of the substance can be improved and the structural faults thereof can be decreased. Further, the leaser resistance of the substance can be also improved.

15 [0020]

The treated substance as defined in claim 11 is obtainable by treating with the process of treating a substance as defined in any one of claims 4 to 10. The treated substance as defined in claim 11, i.e. the fluoride thin film, fluoride
20 powder, fluoride solid or fluoride optical element, is a fluoride having a stoichiometric composition by changing with not only compensating the fluorine loss of the substance but also decreasing impurities by means of the process. Additionally, carrying out the fluorination heat treatment,
25 the crystallinity of the substance can be improved, the

structural faults thereof can be decreased, and the leaser resistance of the substance can be also improved.

[0021]

[Embodiment of carrying out the invention]

5 The fluorination heat treatment apparatus according to the embodiments of the present invention will be described with reference to the drawings hereinafter. An embodiment such that using a fluoride optical element equipped with a fluoride thin film as a substance for treatment, fluorination heat treatment
10 is carried out will be described.

[0022]

Fig. 1 is a block diagram of a fluorination heat treatment apparatus according to an embodiment of the present invention. In Fig. 1, numeral 1 is a fluorine gas storage and feeding vessel
15 made of a Monel alloy of nickel-copper alloy. The fluorine gas storage and feeding vessel 1 is connected with one end of a gas feeding tube 2 made of Monel alloy (fluorine gas feeding tube). Further, the other end of the gas feeding tube 2 is connected with a reactor 3.

20 [0023]

The gas feeding tube 2 is equipped with nickel-plated valves 4, 5, 6 and is connected with a helium gas bomb 7 for feeding a helium gas through the bulb 5 so as to dilute fluorine gas. Controlling the valves 4, 5, 6, fluorine gas, helium gas
25 and a fluorine/helium mixed gas are fed from the fluorine gas

storage and feeding vessel 1 through the gas feeding tube 2 to the reactor 3.

[0024]

The reactor 3 is made of nickel having a purity of not less than 99 %, and an optical element-fixing jig 8 made of nickel having a purity of not less than 99 % is provided inside of the reactor. On the optical element-fixing jig 8, a fluoride optical element 10 coated with a fluorine-lacking fluoride optical thin film 9 is fixed. Further, a temperature measuring thermocouple 11 is provided on the upper part of the reactor 3. Furthermore, a PID controllable external heater 12 is provided on the outer periphery of the fluorine gas storage and feeding vessel 1 and the reactor 3.

[0025]

The reactor 3 is connected with one end of an exhaust tube 13, and the exhaust tube 13 is connected with a valve 14 and a pressure gage 15, a flow rate and pressure controller 16 and a fluorine removing apparatus 17 which constitute an exhaust system. The exhaust tube 13 from the reactor 3 to the valve 14 is made of Monel alloy and nickel plating is applied on the gas contacting part of the valve 14.

[0026]

In this fluorination heat treatment apparatus, the fluorine gas storage and feeding vessel 1 is made of Monel alloy of nickel-copper alloy, the gas feeding tube 2 and the parts

from reactor 3 to valve 14 in the exhaust tube 13 are made of Monel alloy, the gas contacting parts of the valves 4,5,6,14 are plated with nickel and the reactor 3 and the optical element fixing jig 8 are made of nickel having a purity of not less than 5 99 %. Namely, in the region from the fluorine gas storage and feeding vessel 1 to the valve 14, all the parts which contact with fluorine gas are composed of materials having a chromium concentration and a titanium concentration of not more than 1 %, preferably not more than 1000 ppm, more preferably not more than 10 100 ppm.

[0027]

In the fluorination heat treatment apparatus according to the embodiment, the fluorine gas storage and feeding vessel 1, the gas feeding tube 2, the reactor 3 and the optical 15 element-fixing jig 8 are composed of the materials having a chromium concentration and a titanium concentration each of not more than 1 %. In the fluorine gas storage and feeding vessel 1, the gas feeding tube 2, the reactor 3 and the optical element fixing jig 8, the materials of at least parts which actually 20 contact with fluorine gas desirably have a chromium concentration and a titanium concentration each of not more than 1 %.

[0028]

The fluoride thin film formed in the fluoride optical 25 element comprises at least one selected from the group

consisting of magnesium fluoride, calcium fluoride, lithium fluoride, lanthanum fluoride, aluminum fluoride, neodymium fluoride, gadolinium fluoride, yttrium fluoride, dysprosium fluoride, barium fluoride, sodium fluoride, bismuth fluoride, 5 strontium fluoride, lead fluoride, selenium fluoride, cryolite and chiolite.

[0029]

Usable examples of the fluorine fed from the fluorine gas storage and feeding vessel 1 may include a pure fluorine gas; 10 a fluorine gas diluted with at least one rare gas of helium, neon, argon, krypton and xenon; a fluorine atom which is liberated during the treatment from the inner surface of the reactor previously fluorinated; a fluorine atom which is liberated during the treatment from a previously fluorinated 15 metal, a fluorine-excess alloy or a fluorine-excess fluoride placed in the reactor; a fluorine gas generated by electrolysis of a metallic fluoride; a gas obtained by sublimating or evaporating a fluorine-rare gas compound such as XeF_2 , XeF_4 or XeF_6 and a fluorine gas generated by decomposition of the 20 fluorine-rare gas compounds; and an active fluorine of fluorine radical or fluorine ion generated by dissociating at least one of a carbon-fluorine compound, a sulfur-fluorine compound and a nitrogen-fluorine compound.

[0030]

Next, the fluorination heat treatment of the fluorine lacking fluoride thin film-coated fluoride optical element using this fluorination heat treatment apparatus is described. At first, a fluorine type gas is introduced into the reactor 3 and heated to fluoride the inner wall of the reactor 3 and the optical element-fixing jig 8, and thereby nickel fluoride is deposited on the surface to perform passivation.

[0031]

The fluorination heat treatment comprises a first step of placing a substance, a second step of moisture removing with deaeration in the reactor, a third step of fluorination reaction treatment, a fourth step of heat treatment, a fifth step of cooling treatment and a sixth step of withdrawal of the treated substance.

[0032]

In the first step (placing the substance for treatment), the fluoride optical element 10 with the fluoride thin film previously formed is prepared. The fluoride optical element 10 is cleaned and then is fixed to the optical element-fixing jig 8 in the reactor 3.

[0033]

In the second step (moisture removing with deaeration inside the reactor), the reactor 3 is evacuated to 10^{-5} Pa by means of the exhaust system, moisture is removed with deaeration by heating the reactor 3 until 150°C by means of the

external heater 12 for 12 hours, while passing helium gas into the reactor 3 through the gas feeding tube 2. The temperature is measured using the temperature-measuring thermocouple 11. In the moisture removing with deaeration step, the temperature
5 in the reactor 3 may be from 100 to 170°C.

[0034]

In the third step (fluorination reaction treatment), the temperature in the reactor 3 is set at 100°C, and the fluorine gas fed from the fluorine gas storage and feeding vessel 1 is
10 diluted with helium gas to have a desired concentration (1000 ppm to 100%) and is introduced into the reactor 3 through the gas feeding tube 2 and the valve 6 to promote fluorination reaction. Using the flow control and pressure control device 16 provided on the downstream side of the reactor 3, a pressure
15 gage 15 is controlled so as to indicate a desired value (prescribed total pressure and fluorine partial pressure), and the timing is started. In this step, the reactor may be an open reactor wherein the exhaust system is opened to continuously feed the gas or a closed reactor wherein the exhaust system is
20 closed to stop the gas. During the fluorination reaction, the reactor 3 is kept at a constant temperature of 100°C. This condition is kept for a given period of time. In the fluorination reaction treatment, the temperature in the reactor 3 may be from 10 to 150°C.

25 [0035]

In the fourth step (heat treatment), the fluorine gas in the reactor 3 is temporarily exhausted and purged with a helium gas. Once again, fluorine gas fed from the fluorine gas storage and feeding vessel 1 is diluted to have a desired concentration with a helium gas and is again introduced into the reactor 3 through the gas feeding tube 2 and the valve 6. The concentration of the diluted fluorine gas introduced into the reactor 3 in this step is made lower than that of the dilute fluorine gas in the third step (fluorination reaction treatment). The temperature in the reactor 3 is raised up to 300°C, i.e., temperature higher than the temperature in the reactor 3 in the fluorination reaction step. After the temperature is reached to 300°C, by the use of the flow rate and pressure controller 16 provided on the downstream side of the reactor 3, the indicated value of the pressure gage 15 is regulated to be a desired value, and the timing of the heat treatment is started. In this step, the reactor may be an open reactor wherein the exhaust system is opened to continuously let the gas flow or a closed reactor wherein the exhaust system is closed to stop the gas flow. During the heat treatment, the reactor 3 is kept at a constant temperature of 300°C. This condition is kept for a given period of time.

[0036]

In the fifth step (cooling), heating of the reactor 3 is stopped, and cooling of the reactor 3 is started with keeping

the same fluorine concentration as that in the fourth step (heat treatment). When the temperature in the reactor 3 is lowered to 150°C, introduction of the diluted fluorine gas is stopped, and the reactor 3 is evacuated and purged with a helium gas.

5 When the temperature in the reactor 3 is lowered to room temperature, cooling is finished. In the cooling step, the reactor may be an open reactor wherein the exhaust system is opened to continuously let the gas flow or a closed reactor wherein the exhaust system is closed to stop the gas flow.

10 [0037]

In the sixth step (withdrawal of the substance), purging with the helium gas is stopped, and the reactor 3 is released and the substance subjected to the fluorination heat reaction is taken out of the reactor.

15 [0038]

In third step (fluorination reaction), the substance is fluorinated by removing oxygen, hydroxyl groups and other impurities and becomes a fluoride having a stoichiometric composition by completely fluorinating the fluorine-lacking
20 regions of the substance.

[0039]

In the subsequent fourth step (heat treatment), chemical bonding between fluorine and a non-fluorine element is stabilized. Particularly when the substance is a thin film or
25 a porous substance, the structure of the whole substance is

densified by heating to decrease the area exposed to the atmosphere, and after the treatment, when the substance is exposed to the atmosphere, deterioration caused by the reaction with moisture or the like can be markedly reduced.

5 [0040]

The time for the fluorination reaction step and the time for the heat treatment step are sufficiently capable of subjecting the thickness of the prepared thin film or powder to fluorine diffusion at the selected fluorine gas pressure and
10 the selected treating temperature. From the experiments heretofore made, it has been found that the favorable time for each of the steps is about 1 hour. The substance prepared in the first to the sixth steps, i.e., the fluorination treated substance is a fluoride having a stoichiometric composition in
15 which the fluorine loss is compensated and impurities are decreased. Further, the substance has enhanced crystallinity, decreased structural faults and improved laser beam resistance.

[0041]

20 In this embodiment, the case where fluorination heat treatment of a fluoride optical element is carried out using, as a substance, a fluoride thin film-formed fluoride optical element is described. Additionally, fluorination heat treatment of a fluoride thin film, a fluoride powder or a

fluoride solid may be carried out using, as a substance, a fluoride thin film, a fluoride powder or a fluoride solid.

[0042]

Example 1

5 In this example 1, a monel metal alloy of a nickel-copper alloy was used for a material of a section from a reactor 3 to a valve 14 in a gas feeding tube 2 and an exhaust tube 13. Stainless steel valves 4, 5, 6 and 14 were dismantled and gas-contacting portions of the valves were subjected to
10 nickel-plating so that chromium and fluorine were not contacted. By the nickel-plating, the whole fluorine gas feeding system and reaction system were completely chromium free. Samples prepared by film forming each of MgF_2 and LaF_3 single layer films in a film thickness of 150 nm onto a fluorite substrate
15 were used. In a fluorination reaction step at 100°C , 100% fluorine gas was fed. That is, dilution with helium was not conducted. In a subsequent heating step at 300°C , fluorine gas containing 10 ppm of fluorine prepared by diluting with helium gas was introduced. The total pressure in the reactor was
20 determined to 0.1 MPa, i.e. atmospheric pressure from the fluorination reaction step to the heating step.

[0043]

Difference in film loss before and after the fluorination reaction (fluorination with heat) and a chromium concentration
25 detected from the MgF_2 film surface after the fluorination

reaction were shown in Fig. 2. The optical loss used herein was a value determined by measuring a transmittance $T(\%)$ and a reflectance $R(\%)$ in a F_2 laser wavelength (157 nm) and then subtracting them from 100%, i.e. $100 - (T+R)(\%)$. The value of difference in film loss before and after the fluorination reaction is a value determined by subtracting an optical loss before the fluorination reaction from an optical loss after the fluorination reaction. When the value of the difference is negative, this means the fact that the optical loss can be decreased by the fluorination reaction. Contrarily, when the value is positive, this means the fact that the optical loss is increased only by the fluorination reaction. Meanwhile, the chromium concentration was determined by making good use of time of flight secondary ion mass spectrometry (TOF-SIMS), which is suitable for very slight amount elemental analysis.

[0044]

In any of the MgF_2 and LaF_3 films, the difference in the film loss had a negative value and the film loss could be successfully decreased vastly by the fluorination heat reaction. Further, the chromium concentration detected from the MgF_2 film surface was slightly 13 ppm. The titanium concentration detected from the MgF_2 film surface in the same method as the chromium concentration was 20 ppm. The reason that the chromium concentration and the titanium concentration were detected in Example 1 was that the concentrations of metals

other than chromium and titanium were very low and thereby they have no problem.

[0045]

Next, with regard to the LaF_3 film obtained before the fluorination heat treatment and the LaF_3 film obtained after the fluorination heat treatment with the experimental apparatus of Example 1, the O atom concentration and OH concentration in the direction of a film depth were measured by SISM and the results are shown in Fig. 3. In this measurement, the analysis in the depth direction was carried out while sputtering the film with irradiation of plus ions accelerated on the film. The sputtering time in the horizontal axis of the graph meant the depth direction of the film. With prolonging the sputtering time, it indicated information in a deeper position of the film. The sputtering time 0 s indicated in the left end of the graph was namely the film surface, and the sputtering time indicated in the right end of the graph was the deepest position of the film, which was the interface with the substrate. Between before and after the fluorination heat treatment, the O concentrations and the OH concentrations had no difference only on the film surface (sputtering time 0 s). When the fluorination heat treatment was applied on the film, the O concentration was lowered to be one tenth as much as that before the fluorination heat treatment on the whole region of the film inside and the OH concentration was lowered to be one

hundredth. The film was completely fluorinated and thereby the concentrations of oxygen and hydroxyl groups, which induce absorption in the vacuum ultraviolet region, could be decreased remarkably as shown in Fig. 3. Therefore, such a remarkable
5 decrease in the film loss could be attained as shown in Fig. 2.

[0046]

In Example 1, the materials of the valves 4, 5, 6 and 14 were changed from mere stainless steel to stainless steel
10 plated with nickel and the nickel-plated stainless steel was used for the gas-contacting parts located inside of the valves so that great results could be obtained. Besides, in place of the valves prepared by using the nickel-plated stainless steel, the use of valves especially prepared by using monel metal alloy,
15 nickel, nickel alloy, aluminum, aluminum alloy, copper or copper alloy attains the same results.

[0047]

Comparative Examples 1 and 2

In Comparative Example 1, fluorination heat treatment
20 was carried out using a stainless steel gas pipe and a stainless steel valve in the fluorine gas feed system. In Comparative Example 2, fluorination with heat was carried out by changing a material of a gas pipe from stainless steel to monel metal alloy and only using a stainless steel valve (in this case, the
25 stainless steel had a chromium concentration of 18 %) in the

fluorine gas feed system. In Comparative Examples 1 and 2, samples prepared by film forming each of MgF_2 and LaF_3 single layer films in a film thickness of 150 nm onto a fluorite substrate were used. In a fluorination reaction step at 100
5 °C, 100% fluorine gas was introduced. That is, dilution with helium was not conducted. In a subsequent heating step at 300 °C, fluorine gas containing 10 ppm of fluorine prepared by diluting with helium gas was introduced. The total pressure in the reactor was set to 0.1 MPa, i.e. atmospheric pressure
10 from the fluorination reaction step to the heating step.

[0048]

Difference in optical loss of each of the MgF_2 and LaF_3 films before and after the fluorination heat treatment and a chromium concentration detected from the MgF_2 film surface
15 after the fluorination heat treatment were shown in Fig. 2.

In results, as is clear from Fig. 2, in both of Comparative Examples 1 and 2, the optical loss of each of the samples with the MgF_2 and LaF_3 films did not decrease. It rather increased. However, in Comparative Example 2 in which the gas
20 pipe material was changed to monel metal alloy and the stainless valve was used as it was, the increased quantity of the optical loss was lower than that in Comparative Example 1.

Further, in Comparative Example 1, the chromium concentration detected from the MgF_2 film surface after the
25 fluorination heat treatment was 30,000 ppm. In comparative

Example 2, the chromium concentration was 3,000 ppm. It was found by the TOF-SIMS analysis in the film depth direction that in any of the MgF_2 films in Comparative Examples 1 and 2, chromium was deposited on only the surface and was almost absent inside the film. Briefly, it may be concluded that during the fluorination heat treatment, chromium was generated and deposited on the film surface thereby increasing the optical loss. Further, the titanium concentration detected from the MgF_2 film surface after the fluorination heat treatment with the same method as in the detection of the chromium concentration was 80 ppm in Comparative Example 1 and the titanium concentration in Comparative Example 2 was 75 ppm. [0049]

[Consideration]

The reason that Comparative Example 1 and Comparative Example 2 had the above-described results is considered as follows.

[0050]

In the first place, it was found out by X-ray photoelectron spectroscopy (XPS) that the bonding conditions of chromium detected from the MgF_2 film surface in Comparative Examples 1 and 2. The chromium on the film surface was present as chromium oxide Cr_2O_3 . It was also found that the film loss increased after the fluorination heat treatment because chromium oxide Cr_2O_3 that absorbed vacuum ultraviolet light and

did not transmit was deposited on the film surface. This chromium oxide Cr_2O_3 was chemically bonded with the fluoride film surface firmly so that only the chromium oxide could not be removed with washing from the fluoride film as it remained.

5 Accordingly, there was no alternative but to remove the chromium oxide and the fluoride film simultaneously with polishing.

[0051]

Further, the present inventors revealed the reason that
10 nevertheless the heat treatment was carried out in a fluorine atmosphere, chromium oxide Cr_2O_3 was deposited on the film surface.

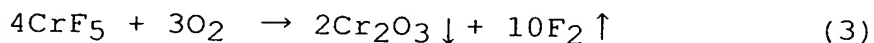
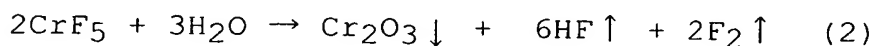
[0052]

F_2 gas is contacted with stainless steel and thereby F_2
15 gas causes chemical reaction, as shown below, together with chromium, which is one element constituting stainless steel to generate chromium fluoride CrF_5 .



This chromium fluoride CrF_5 is a gas so that it was
20 transported to a reactor 3 in a gas stream to adsorb to the inner wall of the reactor 3, a jig for fixing optical elements 8 or the fluoride thin film surface of a fluoride optical element 9. Further, when the fluorination heat treatment is completed and the reactor 3 is released via purging with helium gas, the
25 chromium fluoride CrF_5 gas adsorbed causes chemical reaction,

as shown below, together with atmospheric oxygen gas or water vapor to be solid chromium oxide Cr_2O_3 deposited on the film.



5 On the basis of the no good results of the comparative examples, we found that it is important to remove chromium from the gas-contacting surface and its neighborhood over the whole fluorine gas feeding system and reaction system including from a fluorine gas generating source to the reactor via the gas pipe
10 as much as possible.

[0053]

Example 2

Utilizing the completely chromium-free experimental facility prepared in Example 1, a F_2 lithography antireflection
15 film was fluorinated. With regard to an optical element prepared by forming the antireflection films comprising MgF_2 and LaF_3 alternate layers on the both surfaces of a parallel and plat fluorite substrate having a thickness of 3 mm, the results of measuring a spectral transmittance are shown in Fig.
20 4. It was easily found that the transmittance in the vacuum ultraviolet region of a wavelength of less than 185 nm was really improved by conducting the fluorination with heat according to the present invention. With shortening the wavelength, a marked difference between the conducting of the
25 fluorination with heat or not was recognized. The difference

of the transmittance in the wavelength of 157 nm was 4 %. Only one optical element had a 4 % transmittance difference. Therefore, when all of the optical elements of a semiconductor exposure apparatus comprising several ten sheets of optical
5 element are subjected to fluorination heat treatment according to the present invention, light strength that circuit patterns reaches to a wafer where the circuit patterns are transferred and exposed increases several ten % and exposure properties and throughput can be improved remarkably.

10 [0054]

Furthermore, five sheets of the optical element same as those in Fig. 4 were placed, and measurement of the transmittance thereof was continued with F₂ laser irradiation. The results are shown in Fig. 5. With regard to the optical
15 elements no subjected to fluorination (fluorination with heat), the transmittance decreased together with the number of laser shot. With regard to the optical elements subjected to fluorination, a lowering of the transmission due to laser irradiation could not be observed at all. Specifically, this
20 data discloses that conducting the fluorination of the present invention could vastly reinforce the resistance to vacuum ultraviolet laser light. The O and OH concentrations, which are factors of light absorption in the vacuum ultraviolet region, were vastly decreased so that the laser resistance
25 could be remarkably improved. Therefore, using the

fluorination heat treatment technique of the present invention, it is possible to not only improve the exposure properties and throughput remarkably, but also prolong an optical element life and further to decrease the number of times of maintenance for element change significantly.

[0055]

[EFFECT OF THE INVENTION]

According to the present invention, carrying out the fluorination heat treatment, a fluorine loss of a substance can be compensated and impurities are decreased with the result that the substance can be changed to a fluoride having a stoichiometric composition. Further, carrying out the fluorination heat treatment, the crystallinity of the substance can be improved and structural faults thereof can be decreased. Therefore, an optical absorption edge wavelength is shifted to the shorter wavelength side and approaches that of the ideal crystal, and the absorption attributable to the loss or the impurities is reduced so that the transmittance in the vacuum ultraviolet region is increased, and the laser beam resistance is improved.

[BRIEF DESCRIPTION OF DRAWING]

Fig. 1 is a view of showing a constitution of an experimental apparatus according to an embodiment of the present invention.

Fig. 2 is a graph of showing a film loss change before

and after the fluorination heat treatment in carrying out the fluorination heat treatment with experimental conditions and a chromium concentration detected from the MgF_2 film surface after the fluorination heat.

5 Fig. 3 is a graph of showing results of the O atom concentration and OH concentration in the direction of a film depth measured by SISM with regard to a LaF_3 film obtained before and after the fluorination heat treatment.

10 Fig. 4 is a graph of showing results of measuring a spectral transmittance with regard to an optical element prepared by forming the antireflection films comprising MgF_2 and LaF_3 alternate layers on the both surfaces of a parallel and plat fluorite substrate having a thickness of 3 mm.

15 Fig. 5 is a graph of showing results of measuring a transmittance of five sheets of the optical element same as those in Fig. 4, with F_2 laser irradiation.

[Description of Numeral]

- 1 ... Fluorine gas storage and feeding vessel
- 20 2 ... Gas feeding tube
- 3 ... Reactor
- 4,5,6 ... Valves
- 7 ... Helium gas bomb
- 8 ... Optical element fixing jig
- 25 9 ... Fluoride optical thin film

- 10 ... Fluoride optical element
- 11 ... Thermocouple for measuring temperature
- 12 ... External heater
- 13 ... Exhaust tube
- 5 14 ... Valve
- 15 ... Pressure gage
- 16 ... Flow rate and pressure controller
- 17 ... Fluorine removing device



FIG. 1

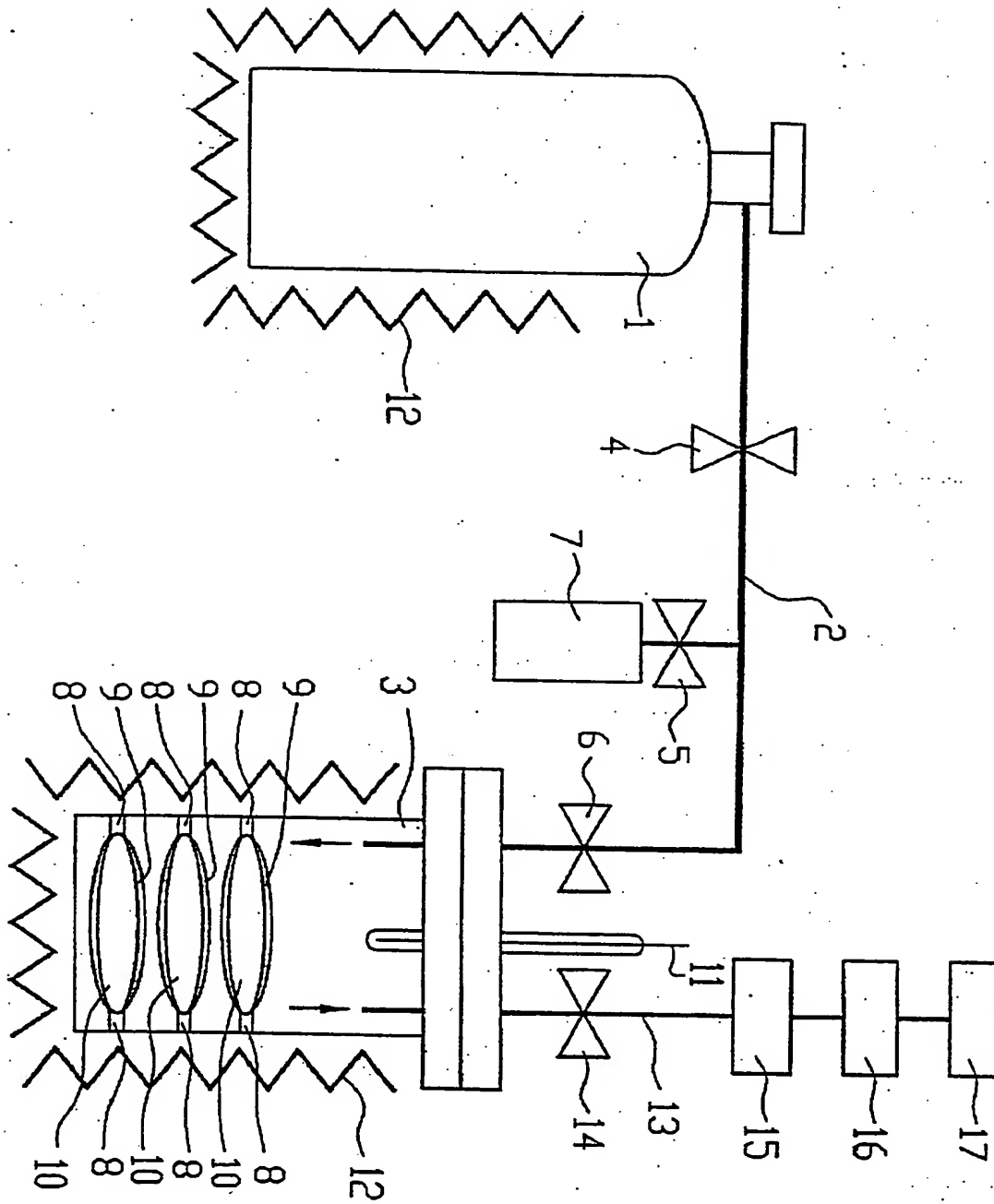
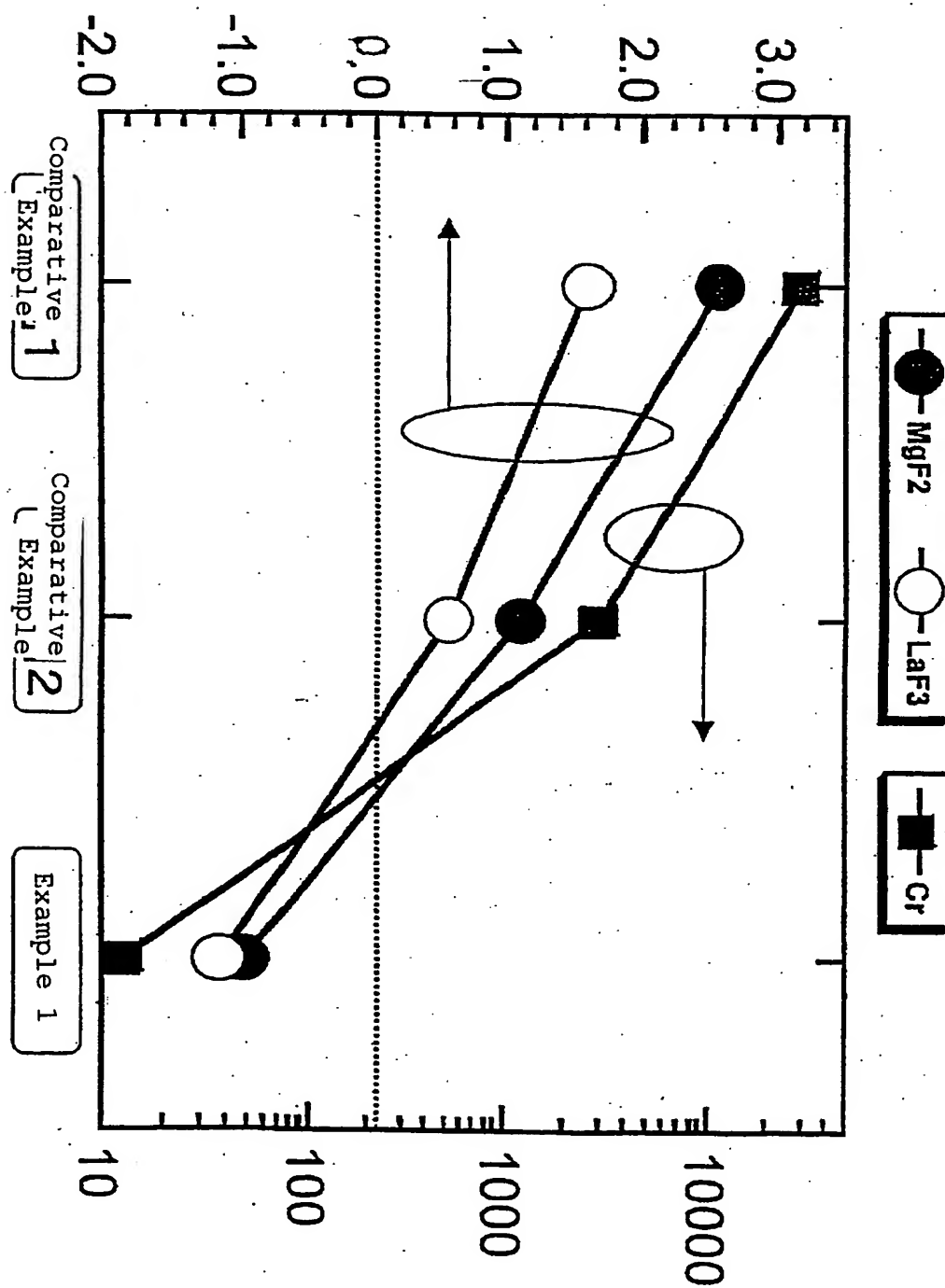




FIG. 2

Optical loss after fluorination heat treatment -
Optical loss before fluorination heat treatment (%)



Chromium concentration (PPM)



FIG. 3

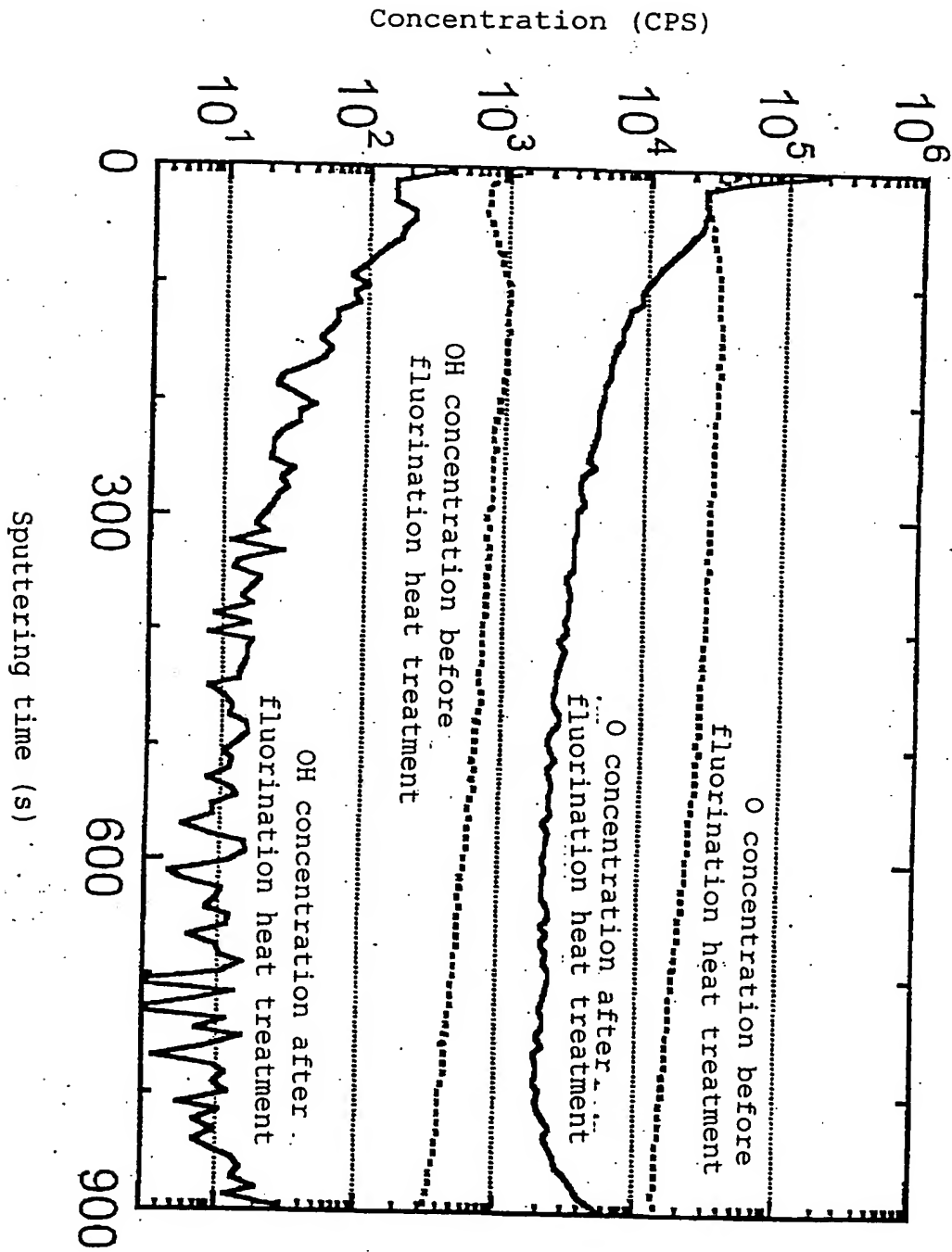




FIG. 4

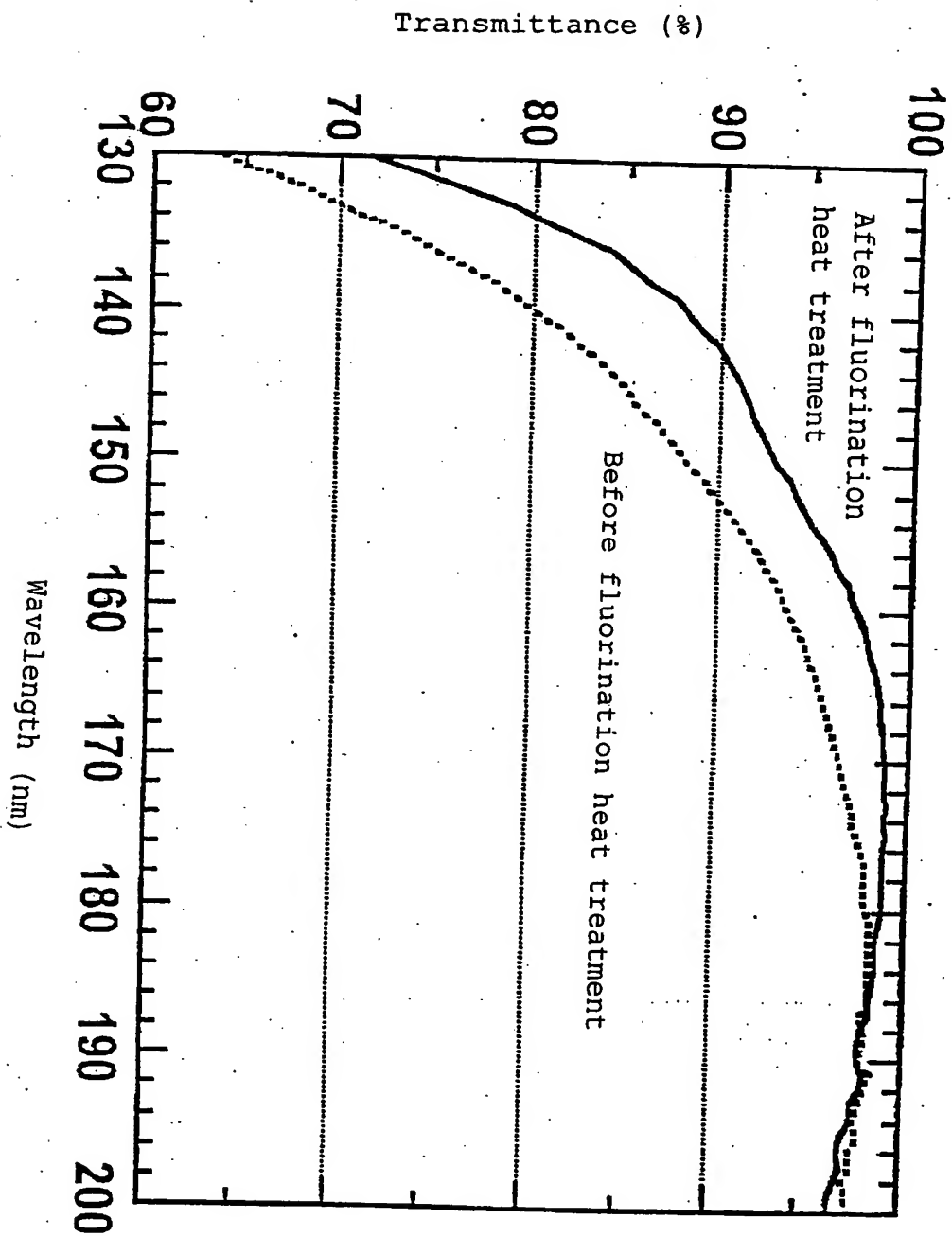
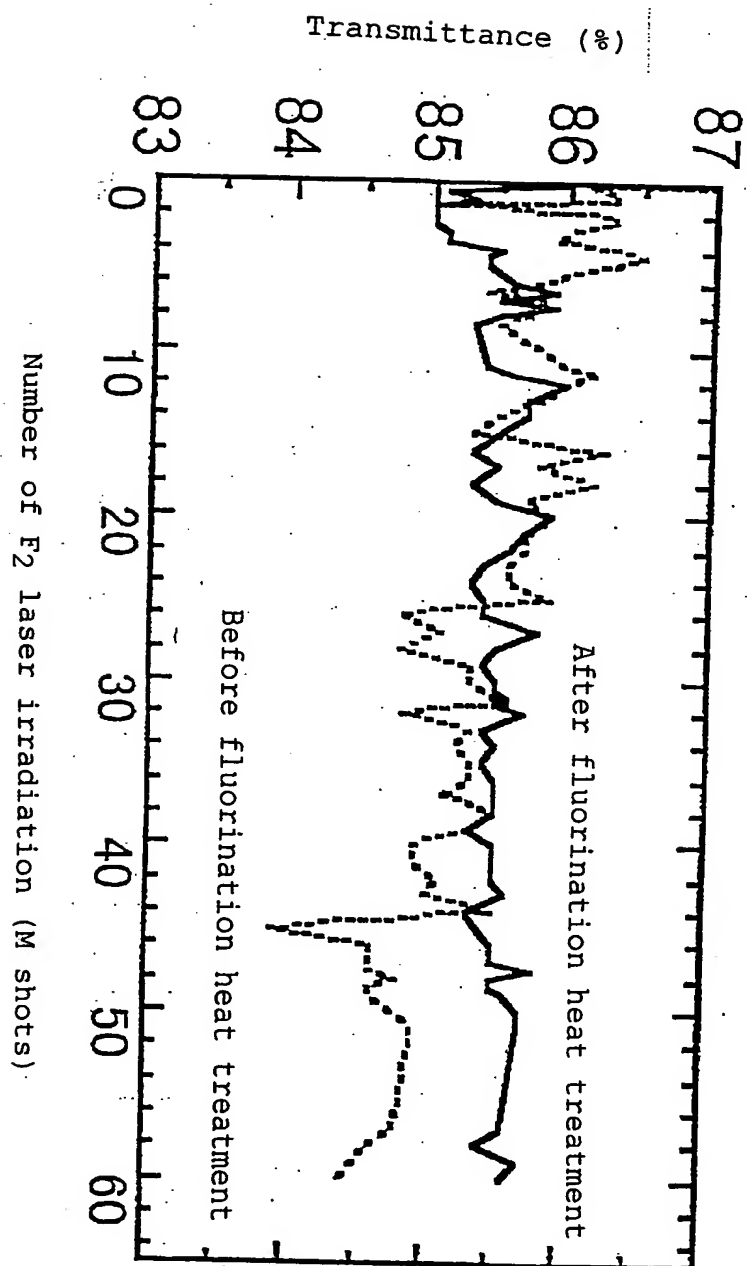




FIG. 5



DECLARATION



I, Yayoi HONDA, c/o S.SUZUKI & ASSOCIATES, 13-6,
Nishigotanda 7-chome, Shinagawa-ku, Tokyo, Japan, do solemnly
and sincerely declare that I understand the Japanese language
and the English language well, and that the attached English
version is a full, true and faithful translation made by me
of the US Provisional Application No. 60/473,890 (May 29, 2003).

I make this solemn declaration conscientiously believing
the same to be true.

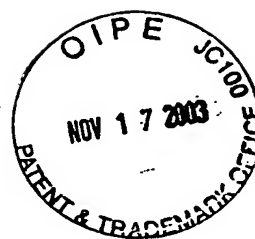
November 7, 2003

Yayoi Honda
Yayoi HONDA

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60/473,890

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[Name of document] Specification

[Title of Invention]

PROCESS FOR TREATING FLUORIDE OPTICAL THIN FILM WITH
DENSIFICATION AND FLUORIDE OPTICAL ELEMENT

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a process for treating a fluoride optical thin film with densification and to a fluoride optical element equipped with a optical thin film densification-treated by the process.

[0002]

[Background of the Invention]

There are semiconductor exposure apparatuses using KrF excimer laser having an ultraviolet wavelength (248 nm) and ArF excimer laser having a deep ultraviolet wavelength (193 nm) as an exposure light source. Optical elements, such as lens, mirror and prism, which are used in an optical system of these semiconductor exposure apparatuses, are placed in a lens barrel, and in the lens barrel, a nitrogen gas is passed through. These optical elements are usually coated with optical thin films such as anti-reflection films, high reflection films and semi-transmission films.

[0003]

The optical element material itself is synthesized using, as starting materials, a high-purity powder and a reactive gas at a high temperature of not lower than 1000°C in order to sufficiently promote the chemical reaction. After the synthesis, the optical element material is gradually cooled over a sufficient period of time and then subjected to annealing if desired, so that impurity elements, faults and strains which may cause light absorption or scattering are removed to the utmost from the optical element material. Further, scattering on the optical element surface is remarkably decreased with the development of polishing technique.

[0004]

The optical thin film is readily formed at a relatively lower temperature by various PVD methods such as vacuum deposition using resistance heating or electron beam dissolution, vacuum deposition with ion assist, ion plating, sputtering, and ion beam sputtering. The optical thin film must be formed only by heating the optical element as a substrate at a relatively lower temperature because high-temperature heating causes heat distortion of the optical element to thereby produce deviation of the dimensional accuracy of the optical element surface, and desired image-formation properties are not attained.

[0005]

By the way, the optical element material formed at a high temperature over a long period of time is a densified bulky solid and has no voids at all through which various gaseous molecules enter. The optical thin film formed on the optical element at a relatively lower temperature as described above has a porous structure having many pores and voids and a very large specific surface area, so that very large amounts of water vapor, volatile organic substances and volatile inorganic substances enter and are adsorbed inside. Most of volatile organic substances and volatile inorganic substances absorb light of ultraviolet KrF excimer laser wavelength and light of deep ultraviolet ArF excimer laser wavelength. Further, light of the vacuum ultraviolet F₂ laser wavelength (157 nm) used as an exposure light source of a semiconductor exposure apparatus for the next generation is absorbed even by water vapor.

[0006]

In the semiconductor exposure apparatus, a nitrogen gas is passed through the lens barrel in which the optical element is placed, however, trace amounts of volatile organic substances, volatile inorganic substances such as ammonia and water vapor contained in the environment of arranging the semiconductor exposure apparatus and the nitrogen gas are unfavorably introduced into the lens barrel. The volatile organic substances, volatile inorganic substances and water vapor introduced into the lens barrel adhere onto the optical

thin film formed on the optical element surface and enter the optical thin film deeply through the voids or pores of the film and are adsorbed to cause light absorption. After the laser irradiation, these substances are polymerized or adhered strongly to decrease the light transmittance.

[0007]

A reduction projection semiconductor exposure apparatus is provided with several tens of optical elements of various shapes and purposes between a laser light source and a wafer in which the semiconductor circuit is exposed, and on the both surfaces of the optical elements, i.e., both surfaces of the light incidence side and the light outgoing side, are coated with optical thin films. That is to say, the number of the surfaces coated with the thin film is twice the number of all of the optical elements. In one semiconductor exposure apparatus, the optical elements used are all arranged in the same lens barrel, so that they are almost equally contaminated with the volatile organic substances, volatile inorganic substances and water vapor and are lowered in the light transmittance. If the transmittance of one side coated surface of a certain optical element is defined as T and a decreased amount of the transmittance by contamination is defined as ΔT , the both-side transmittance of the optical element after contamination is represented by $(T-\Delta T)^2$. If the number of all the optical elements is defined as n , a decreased amount of the

transmittance in the whole system is represented by $(T - \Delta T)^{2N}$. Therefore, if the optical elements are contaminated, the quantity of light which transmits all of the several tens of optical elements from the laser light source and reaches the wafer surface absolutely becomes small as compared with the ideal case where the optical elements are not contaminated at all. As a matter of course, it is impossible to completely remove volatile organic substances, volatile inorganic substances and water vapor introduced into the lens barrel although efforts to minimize the introduction thereof into the lens barrel are made, so that a lowering of transmittance attributable to adsorption, polymerization or adhesion of volatile organic substances, volatile inorganic substances and water vapor is an inevitable problem. After all, the quantity of light reached to the wafer surface through all the optical elements becomes extremely small, e.g., about several % of the original quantity of the light emitted from the light source. On this account, the exposure time is prolonged, and the frequency of changes of optical elements is increased when polymerized products are thickly deposited with the result that the productivity is markedly lowered.

[0008]

It is an object of the present invention to provide a process for treating a fluoride optical thin film with densification, more particularly a process for densifying a

structure of an optical thin film deposited on an optical element, and to provide a fluoride optical element having a fluoride optical thin film densified with the process.

[0009]

[Means for the solving the Object]

The process for treating an optical thin film with densification as described in claim 1 comprises the step of

placing a fluoride optical element laminated with a fluoride optical thin film in a reactor ,

conducting densification by introducing a fluorine gas into the reactor and heating the fluoride optical thin film,

cooling the fluoride optical element placed in the reactor, and

taking out the fluoride optical element from the reactor wherein the temperature in the reactor is from 200 to 400°C and the fluorine gas concentration is from 10 ppm to 100 %, in the densification.

[0010]

According to the process for treating an optical thin film with densification as described in claim 1, a loss of fluorine of the fluoride optical thin film laminated on the fluoride optical element can be compensated and also the fluoride optical thin film can be densified. Therefore, in a semiconductor exposure apparatus holding an optical element, it is possible to minimize a lowering of a transmittance (fogging) of the

fluoride optical thin film caused by absorption or polymerization of volatile organic substances and volatile inorganic substances remained in a lens barrel with the fluoride optical thin film.

[0011]

The fluoride optical element as described in claim 2 is characterized in that by carrying out the process for treating a fluoride optical thin film with densification, it has a fluoride optical thin film having pores, through which water vapor, volatile organic substances and volatile inorganic substances can enter, being closed.

[0012]

In the fluoride optical element as described in claim 2, the pores, through which water vapor, volatile organic substances and volatile inorganic substances can enter, are closed and the fluoride optical thin film is densified. Therefore, the fluoride optical element equipped with the fluoride optical thin film which can minimize a lowering of a transmittance (fogging) caused by absorption or polymerization of volatile organic substances and volatile inorganic substances with the fluoride optical thin film can be prepared.

[0013]

[Embodiment of carrying out the Invention]

Hereinafter, the process for treating an optical thin film with densification according to one embodiment of the

present invention will be described with referring to the drawings.

[0014]

Fig. 1 is a structural diagram of showing a densification treating apparatus for an optical thin film according to one embodiment of the present invention. The densification treating apparatus is equipped with a reactor 2 having a cylindrical inner space in which an optical element laminated with an optical thin film is placed, and an outer heater 4 is disposed around the reactor 2. A gas inlet 6 and a valve 8 which opens or closes the gas inlet 6 are provided on the bottom of the reactor 2. A gas outlet 10, a valve 12 which opens or closes the gas outlet 10 and a flow rate and pressure controller 14 which controls the flow rate of exhaust gas and also controls the inside pressure of the reactor 2 are provided on the upper part of the reactor 2.

[0015]

In the inside space of the reactor 2, plural optical element supports 16 for supporting the optical elements are provided and each optical element support supports a fluoride optical element 18 formed from fluorite. Each fluoride optical element 18 is laminated with a fluoride optical thin film 20. In the vicinity of the optical element supports 16 in the reactor 2, nickel made thermo-couple inserting tubes 22 are provided and thermo-couples 24 for measuring the fluorine

gas atmosphere temperature in the reactor each are inserted into each of the thermo-couple tubes 22.

[0016]

Next, the process for treating the fluoride thin film with densification using the densification treating apparatus for the optical thin film is described. The material of the reactor 2 is nickel, and the materials of valve 8, valve 12 and gas feeding tube are Monel metals of nickel-copper alloy. The materials of the inner wall of the reactor 2, the inner wall of the gas feeding tube and the gas contacting parts of the valve 8 and the valve 12 may be selected from at least one of nickel, nickel alloy, copper, copper alloy, aluminum and aluminum alloy and the materials also have a chromium concentration and titanium concentration of not more than 1 %, preferably not more than 1000 ppm, more preferably not more than 100 ppm.

[0017]

In the first step of the optical thin film densification treatment (placing step), fluoride optical elements 18 with the fluoride optical thin film 20 formed previously are prepared. The prepared fluoride optical elements 18 are cleaned and then are fixed to each of the optical element supports 16 in the reactor 2.

[0018]

In the second step (deaeration treating step), using a vacuum pump, the reactor 2 is evacuated through the gas outlet

10 until the inside pressure of the reactor 2 is 10^{-4} Pa. Thereafter, while helium gas is introduced into the reactor 2 through the gas inlet 6, the fluoride optical elements 18 placed in the reactor 2 are heated at 150°C using the external heater 4 and held for 12 hr and thereby moisture is removed with deaeration. The temperature of the fluoride optical elements 18 is measured using the thermo-couples 24. The treatment temperature in the moisture removing treatment with deaeration can be selected from 100 to 170°C .

[0019]

In the third step (densification treatment step), a 10 ppm fluorine gas diluted with helium gas is introduced into the reactor 2. While the inside pressure of the reactor 2 is regulated at 1 atm using the flow rate and pressure controller 14 by regulating the dilution fluorine gas flow rate, the temperature in the reactor 2 is elevated to 300°C . The temperature reaches to 300°C and thereafter the timing for the densification treatment is started at a constant temperature of 300°C at a constant pressure of 1 atm. In this densification treatment step, heating is conducted in a fluorine gas atmosphere so that a loss of fluorine is prevented and also the fluoride optical thin films are sintered and thereby densified. In this procedure, an open reactor wherein the vent system is opened and the gas is continuously flown may be used or a closed reactor wherein the vent system is closed and the gas is not

flown may be used. In the densification-treating step, the temperature inside the reactor 2 is appropriately selected from 200 to 400°C and the fluorine gas concentration is appropriately selected from 10 ppm to 100 %.

[0020]

In the fourth step (cooling step), the heating in the reactor 2 is stopped and cooling in the reactor 2 is started at the same fluorine gas concentration as that in the third step. When the temperature in the reactor 2 is lowered to room temperature, introduction of diluted fluorine gas is stopped, and the reactor 2 is evacuated and purged with helium gas. During the cooling step, an open reactor wherein the vent system is opened and the gas is continuously flown may be used or a closed reactor wherein the vent system is closed and the gas is not flown may be used.

[0021]

In the fifth step (taking out step), purging with helium gas is stopped and the reactor 2 is released, and then the fluoride optical elements 18 subjected to the densification treatment are taken out from the reactor.

[0022]

Example 1

A MgF₂ single layer film having a film thickness of 150 nm was deposited on a fluorite substrate with a vacuum deposition method to prepare a sample. The sample was subjected

to densification in accordance with the densification treating process for a fluoride thin film on a fluoride optical element as described in the embodiment of the invention. That is, the sample was cleaned and then was fixed to an optical element support 16 in a treating furnace (reactor) 2 (placing step). Using a vacuum pump, the reactor 2 was evacuated through a gas outlet 10 until the inside pressure of the reactor 2 reached to 10^{-4} Pa and thereafter, while helium gas was introducing through a gas inlet 6 into the reactor 2, the sample present in the reactor 2 was heated to 150°C with an external heater 4, and kept for 12 hr to conduct deaeration for removal of moisture (deaeration treatment step). A thermo-couple 24 was used for measuring the sample temperature.

[0023]

Subsequently, 10 ppm fluorine gas diluted with helium gas was introduced into the reactor 2. While the diluted fluorine gas flow rate was regulated using a flow rate and pressure controller 14 so that the inside pressure of the reactor 2 was 1 atm, and the temperature in the reactor 2 was elevated to 300°C (densification treatment step). After the temperature reached to 300°C , timing for the densification treatment was started and the temperature and the pressure were kept to be 300°C and 1 atm respectively.

[0024]

Next, heating in the reactor 2 was stopped and then cooling

in the reactor 2 was started with keeping the same fluorine gas concentration (cooling step). When the temperature in the reactor 2 lowered to room temperature, the introduction of diluted fluorine gas was stopped and the reactor 2 was evacuated and purged with helium gas. The helium gas purging was stopped and the reactor 2 was released and then the objective sample densification treated was taken out (taking out step).

[0025]

With regard to the MgF_2 single layer film, which was a sample, the cross sectional SEM photographs thereof before and after the treatment are shown in Fig. 2.

From the observation of the cross section of as-depo film before the treatment, it is found that thin pillars were extended from the interface between the substrate and the film toward to the film surface and the film was formed by the thin pillars in a bound state. The as-depo film is a typical pillar structure. Simultaneously, it is easily confirmed that among the thin pillars, there are gaps through which low molecular weight gas can be readily passed. On the surface of each of the thin pillars, a volatile substance can be adsorbed. The primary specific surface area of the film was quite vast as compared with the area of the surface of the film upper portion. Meanwhile, concerning the film treated with densification according to the present invention, it is confirmed that as a result of heating, thin pillars are adhered each other and

thereby each of the pillars is thickened so that the gaps between the pillars are closed or narrowed to change into a minute structure.

[0026]

Example 2

In a semiconductor exposure system, as described above, the inside of a lens barrel holding an optical element was purged with nitrogen gas. It is found from the results of the trace gases analysis that volatile impurities having a possibility that they will enter the lens barrel are oxygen, water vapor, aromatic organic substances, siloxane organic substances or ammonia. Among them, the aromatic organic substances and siloxane organic substances adsorb on the optical thin film surface of the optical element and thereafter, optical CVD reaction is caused by laser irradiation and thereby the substances are polymerized and strongly adhered to lower the transmittance of the optical element. Such a phenomenon that these organic substances are polymerized and strongly adhered on the optical thin film is called as "fogging".

[0027]

The exposure properties and productivity of the exposure apparatus depend on whether the fluoride optical element with the fluoride optical thin film employed in the semiconductor exposure system is easy of causing fogging or difficult of causing fogging. The present inventors artificially made the

circumstances that fogging generates in the fluoride optical element with the fluoride optical thin film. Under the circumstances, the fluoride optical element with the fluoride optical thin film was irradiated with laser and then the transmittance variation thereof was measured. It was confirmed by the experiment that the degree of fogging has large difference according to the structure of the thin film. The experiment process and the results are described below.

[0028]

Fig. 3 is a structural diagram of a laser irradiation experimental apparatus. The apparatus was made for the purpose of irradiating ArF excimer laser on an optical element having a surface laminated with an optical thin film. The apparatus, further, has a structure such that laser irradiation can be conducted by changing the gas circumstances in the chamber holding the optical element or changing the impurity concentration. Therefore, the laser irradiation experimental apparatus is an experimental apparatus capable of obtaining the same results as the case that optical elements such as lens, prism or mirror are held in a lens barrel of an actual semiconductor exposure apparatus.

[0029]

As shown in Fig. 3, ArF excimer laser light emitted from an ArF laser oscillator 30 is introduced into a chamber 36 holding an optical element 34 through an ArF laser optical path

32. That is, ArF excimer laser light is introduced into the chamber 36 through an open-close shutter 38, a waveguide 40 and an incident side fluoride window 42 provided between the ArF laser oscillator 30 and the chamber 36.

[0030]

In the chamber 36, an optical element support 42 for supporting the optical element 34 and on the optical element 34, which is supported by the optical element support 42, an optical thin film 44 is formed. In the chamber 36, an injection side fluoride window 46 is provided and ArF excimer laser light emitted from the emission side fluoride window 46 enters into a joule meter 52 through a waveguide 48 and an open-closed shutter 50. In the chamber 36, a gas feeding tube 54 and an open-close valve 56 which conducts opening and closing the gas introducing tube 54 are provided and also a gas exhaust tube 58 and an open-close valve 58 [sic 60] which conducts opening and closing the gas exhaust tube 58 are provided.

[0031]

First, a sample was prepared by forming a DUV region antireflection film composed of $\text{MgF}_2/\text{LaF}_3$ alternating laminate on the both sides of a parallel and flat fluorite substrate having a thickness of 3 mm. Two sheets of the sample was prepared, and one was put aside as an as-depo film sample without treatment and the other was subjected to densification treatment for a fluoride according to the present invention and

then was taken as a densification treated film sample.

[0032]

With regard to each of the as-depo film sample and the densification treated sample, the transmittance spectrum just before irradiation with ArF excimer laser was measured by a spectral transmittance measuring apparatus. The transmittance spectrums measured are shown in Figs. 4 and 5 respectively.

[0033]

Next, the as-depo film sample was placed in the laser irradiation experimental apparatus as shown in Fig.3. While a mixed vapor composed of toluene typified aromatic organic substances and octamethylcyclotetrasiloxane typified siloxane organic substances was circulated by nitrogen gas in the laser irradiation experimental apparatus, the sample was irradiated with ArF excimer laser at 10^6 shot.

[0034]

Then, the densification treated film sample was placed in the laser irradiation experimental apparatus as shown in Fig. 3. While the same mixed vapor composed of toluene and octamethylcyclotetrasiloxane was circulated by nitrogen gas in the laser irradiation experimental apparatus, the sample was irradiated with ArF excimer laser at 10^6 shot.

[0035]

Lastly, with regard to both samples of the as-depo film

and the densification treated film, after the irradiation with ArF excimer laser, the transmittance spectrums were measured by the spectral transmittance measuring apparatus. The transmittance spectrums measured are shown in Figs. 4 and 5 respectively. In both of the results of Figs. 4 and 5, the transmittance lowered after the laser irradiation and the spectrum was shifted to the long wavelength side. The results show that polymeric products absorbing ultraviolet light are deposited. That is, the transmittance lowered by absorbing light and the polymeric products are deposited on the optical thin film to increase the film thickness and thereby the spectrum is shifted to the long wavelength side.

[0036]

When the as-depo film sample in Fig. 4 and the densification treated sample in Fig. 5 are compared, the densification treated sample has a lowering of the transmittance and shift of the spectrum to the long wavelength side, which are remarkably smaller than those of the as-depo film. According to the densification treatment process of the present invention, by densifying the structure of the optical thin film and removing gaps or pores, impurities cannot enter and cannot adsorb into the film inside through gaps or pores so that a lowering of the transmittance due to polymerized film deposition can be remarkably restrained.

[0037]

When the fluoride optical thin film densified by the densification treatment process according to the present invention is employed in a semiconductor exposure system where ultraviolet KrF excimer laser wavelength, deep ultraviolet ArF excimer laser wavelength, and vacuum ultraviolet F2 laser wavelength are used for an exposure light source, a transmittance lowering (fogging) of the fluoride optical thin film can be depressed extremely. The transmittance lowering is induced by adsorbing and polymerizing volatile organic substances or volatile inorganic substances remained in the lens barrel holding the optical element, with the fluoride optical thin film.

Therefore, a transmittance lowering or occurrence of illuminance non-uniformity can be depressed in baking fine circuit patterns on a semi-conductor wafer and thereby the productivity of the semiconductor exposure system can be remarkably improved.

[0038]

Example 3

The present inventor have been earnestly studied and found that in order to densify the fluoride optical thin film with lowering the optical absorption loss of the fluoride optical thin film, it is necessary to heat the fluoride optical thin film in an atmosphere of fluorine gas. The specific experiment results are shown below.

[0039]

A sample was prepared by forming an antireflection film for use at 157 nm, which film was composed of $\text{MgF}_2/\text{LaF}_3$ alternating laminate, on the both sides of a parallel and flat fluorite substrate having a thickness of 3 mm. The sample was subjected to densification treatment in an atmosphere of fluorine gas in accordance with the process for densification treating a fluoride as described in the embodiment of the invention. That is, the sample was cleaned and then fixed on an optical element support 16 in a treating furnace (reactor) 2 (placing step). Using a vacuum pump, the reactor 2 was evacuated until the inside pressure of the reactor 2 reached to 10^{-4} Pa and thereafter, while helium gas was introduced through a gas inlet 6 into the reactor 2, the sample present in the reactor 2 was heated to 150°C with an external heater 4, and kept for 12 hr to conduct deaeration for removal of moisture (deaeration treatment step). A thermo-couple 24 was used for measuring the sample temperature.

[0040]

Subsequently, 10 ppm fluorine gas diluted with helium gas was introduced into the reactor 2. While the diluted fluorine gas flow rate was regulated using a flow rate and pressure controller 14 so that the inside pressure of the reactor 2 was 1 atm, the temperature in the reactor 2 was elevated to 300°C (densification treatment step). After the temperature reached

to 300°C, timing for the densification treatment was started and the temperature and the pressure were kept to be 300°C and 1 atm respectively.

[0041]

Next, heating in the reactor 2 was stopped and then cooling in the reactor 2 was started with keeping the same fluorine gas concentration (cooling step). When the temperature of the reactor 2 lowered to room temperature, the introduction of diluted fluorine gas was stopped and the reactor 2 was evacuated and purged with helium gas. The helium gas purging was stopped and the reactor 2 was released and then the objective sample densification treated was taken out (taking out step). This sample was called as a film densification treated in a fluorine atmosphere.

[0042]

With regard to the film densification treated in an atmosphere of fluorine, the transmittance spectrum measured by a spectral transmittance measuring apparatus is shown with a solid line in a graph of Fig. 6. The film densification treated in a fluorine atmosphere has a higher transmittance with shortening the wavelength as compared with the as-depo film as described later. This reason was that when the densification reaction is progressed with heating the fluoride thin film in an atmosphere of fluorine, fluorination of the fluoride thin film is simultaneously caused, and thereby fluorine-lack slight

portions present in the fluoride thin film are refilled with fluorine and optical absorbing loss in the vacuum ultraviolet region is decreased.

[0043]

Comparative Example

Two sheets of the sample same as used in Example 3 were prepared. That is, each of two sheets of samples was prepared by forming an antireflection film for use at 157 nm, which film was composed of $\text{MgF}_2/\text{LaF}_3$ alternating laminate, on the both sides of a parallel and flat fluorite substrate having a thickness of 3 mm. One sample was subjected to densification treatment in an atmosphere of helium free from fluorine. That is, this sample was cleaned and then was fixed to an optical element support 16 in a reactor 2 (placing step). Using a vacuum pump, the reactor 2 was evacuated through a gas outlet 10 until the pressure inside the reactor 2 reached to 10^{-4} Pa and thereafter, while helium gas was introduced through a gas inlet 6 into the reactor 2, the sample present in the reactor 2 was heated to 150°C with an external heater 4, and kept for 12 hr to conduct deaeration for removal of moisture (deaeration treatment step). A thermo-couple 24 was used for measuring the sample temperature.

[0044]

Subsequently, while the helium gas flow rate was regulated using a flow rate and pressure controller 14 in an

atmosphere of helium gas completely free from fluorine so that the inside pressure of the reactor 5 was 1 atm, the temperature of the reactor 2 was elevated to 300°C (densification treatment step). After the temperature reached to 300°C, timing for the densification treatment was started and the temperature and the pressure were kept to be 300°C and 1 atm respectively.

[0045]

Next, heating of the reactor 2 was stopped and then cooling of the reactor 2 was started (cooling step). When the temperature of the reactor 2 lowered to room temperature, the reactor 2 was released and then the objective sample densification treated was taken out (taking out step). This sample is called as a film densification treated in an atmosphere of helium.

[0046]

The other sample was subjected to no treatment after the film forming. The sample is called as an as-depo film.

[0047]

With regard to the film densification treated in an atmosphere of helium and the as-depo film, the transmittance spectrum measured by a spectral transmittance measuring apparatus is shown with a broken line in a graph of Fig. 6. The film densification treated in an atmosphere of helium has a remarkably lower transmittance, and the transmittance further lowers with shortening the wavelength as compared with the

as-depo film. The chemical compositions of both of the samples were specifically analyzed using an electron beam probe microanalysis apparatus (EPMA). In results, the fluorine content of the film densification treated in an atmosphere of helium largely lowered as compared with the as-depo film. Namely, when the densification treatment of the fluoride thin film was progressed with heat in an atmosphere of helium gas or the like except for fluorine as in this case, the fluoride thin film was densified but simultaneously, fluorine atom was detached and evaporated from the fluoride thin film. As a result, the fluoride thin film lacked of fluorine greatly and the optical absorbing loss in the vacuum ultraviolet region increased with shortening the wavelength.

[0048]

According to Example 3 and Comparative Example, heating the fluoride optical element with the fluoride optical thin film in an atmosphere of fluorine gas, the fluoride optical thin film can be densified without increasing the optical absorbing loss of the fluoride optical thin film.

[0049]

[Effect of the Invention]

The present invention provides the fluoride optical element with the fluoride optical thin film capable of minimizing a lowering of transmittance (fogging) caused by absorption or polymerization of volatile organic or inorganic

substances remained in the lens barrel holding the optical element with the fluoride optical thin film. Accordingly, employing the fluoride optical element with the fluoride optical thin film densified by the densification treating process for the fluoride optical thin film to a semiconductor exposure apparatus in which KrF excimer laser having an ultraviolet wavelength and ArF excimer laser having a deep ultraviolet wavelength are used as an exposure light source, in baking fine circuit patterns on a semiconductor wafer, a lowering of transmittance or occurrence of illuminance irregularity can be depressed and the productivity of the semiconductor exposure apparatus can be greatly improved.

[Brief Description of Drawing]

Fig. 1 is a structural diagram of showing a densification treating apparatus for an optical thin film

Fig. 2 shows cross sectional SEM photographs of MgF_2 film before and after densification treatment.

Fig. 3 is structural diagram of showing a laser irradiation experimental apparatus.

Fig. 4 shows transmittance spectrums obtained before and after fogging test with ArF excimer laser irradiation on an as-depo film of $\text{MgF}_2/\text{LaF}_3$ alternate-laminated antireflection film laminated on a fluorite substrate.

Fig. 5 shows transmittance spectra obtained before and after fogging test with ArF excimer laser irradiation on $\text{MgF}_2/\text{LaF}_3$ alternate-laminated antireflection film laminated on a fluorite substrate treated with the densification treatment.

Fig. 6 shows transmittance spectra of as-depo film, fluorine atmosphere densification treated film and helium atmosphere densification treated film with regard to $\text{MgF}_2/\text{LaF}_3$ alternate-laminated antireflection film for use at 157 nm laminated on a fluorite substrate.

[Description of Number]

- 2 ... Reactor
- 4 ... External heater
- 6 ... Gas inlet
- 8 ... Valve
- 10 ... Gas outlet
- 12 ... Valve
- 14 ... Flow rate and pressure controller
- 16 ... Optical element support
- 18 ... Fluoride optical element
- 20 ... Fluoride optical thin film
- 22 ... Thermocouple inserting tube
- 24 ... Thermocouple
- 30 ... ArF laser oscillator
- 32 ... ArF laser light path

- 34 ... Optical element
- 36 ... Chamber
- 42 ... Optical element support
- 44 ... Optical thin film
- 52 ... Joule meter

FIG. 1

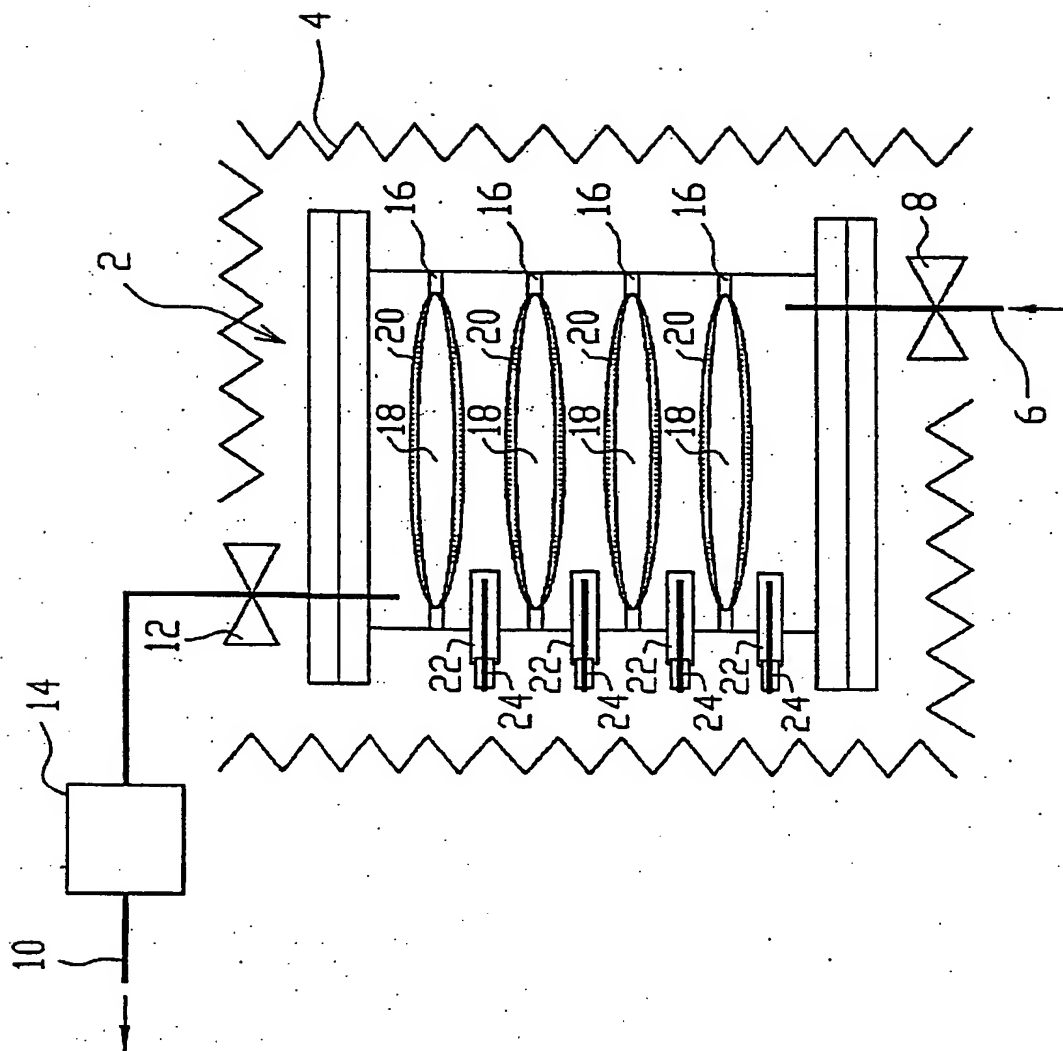


FIG. 2

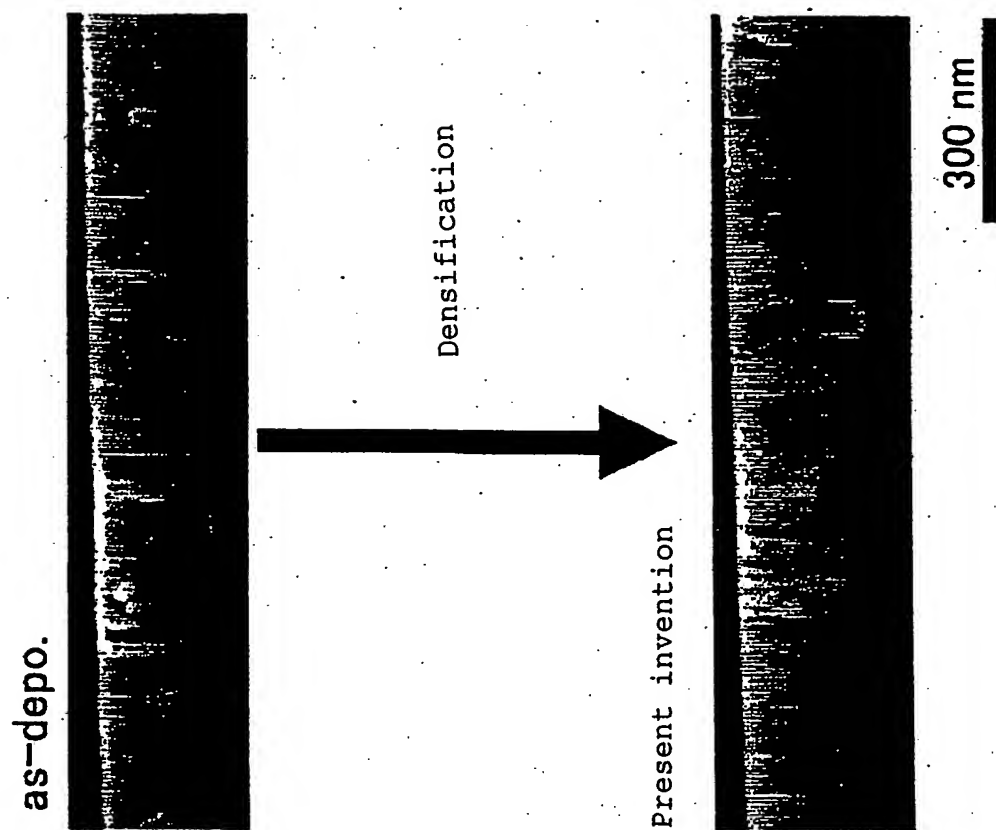


FIG. 3

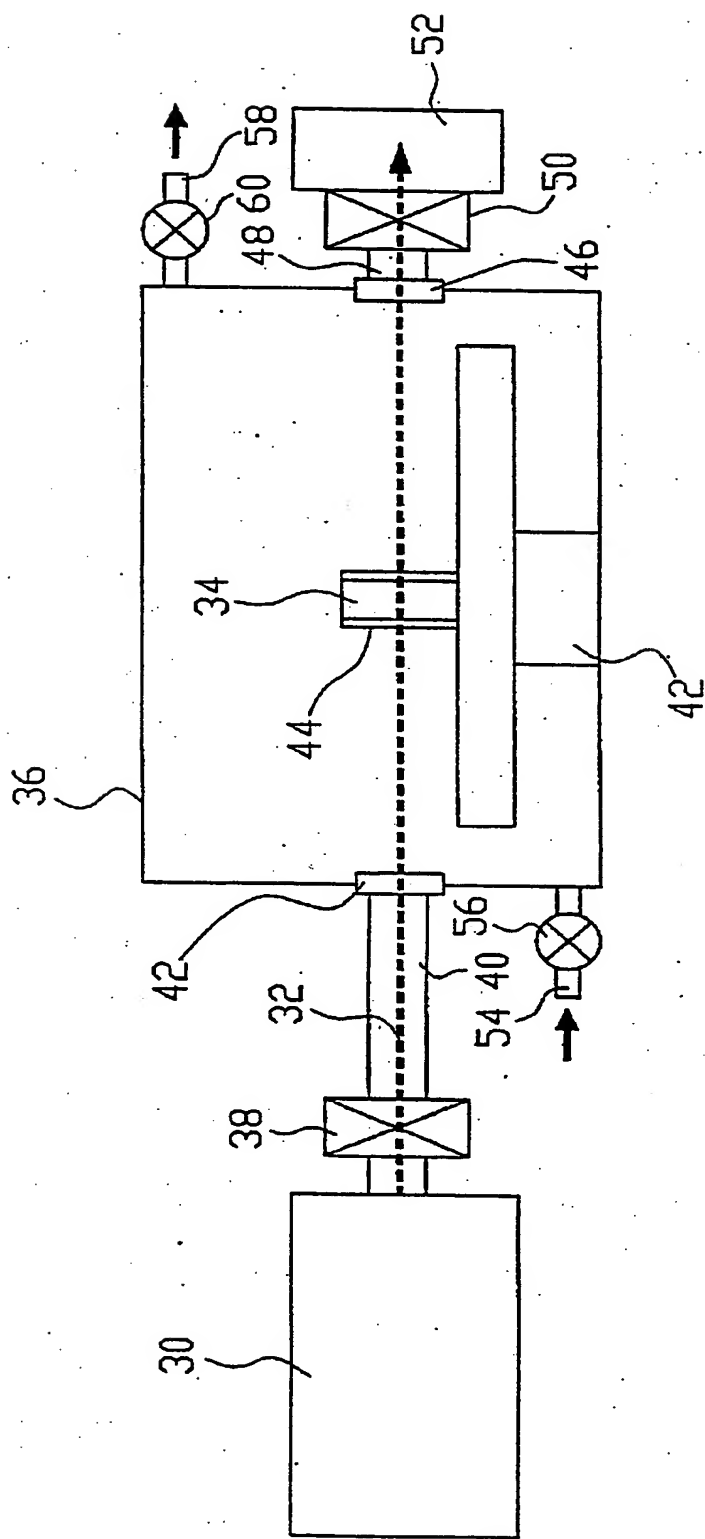


FIG. 4

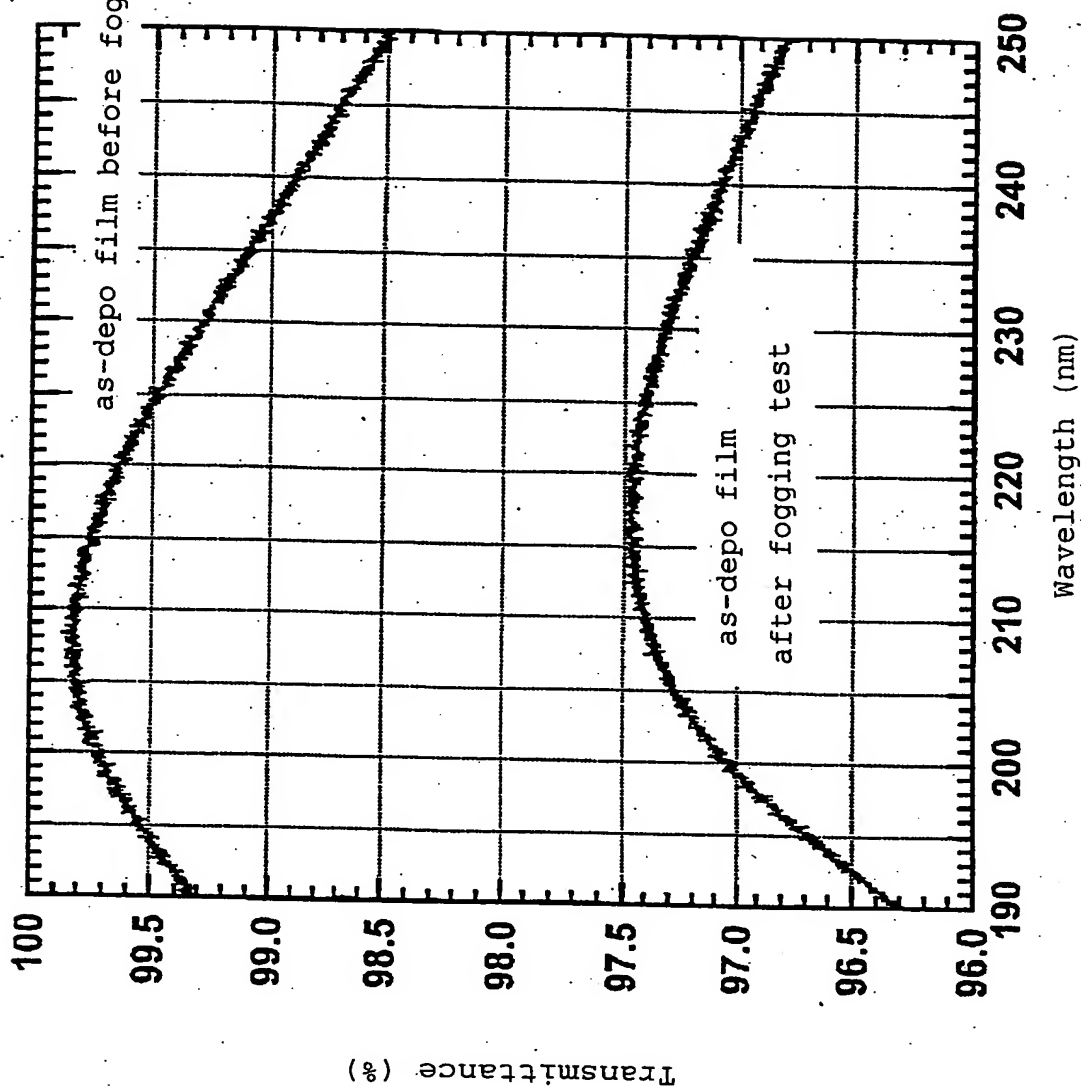


FIG. 5

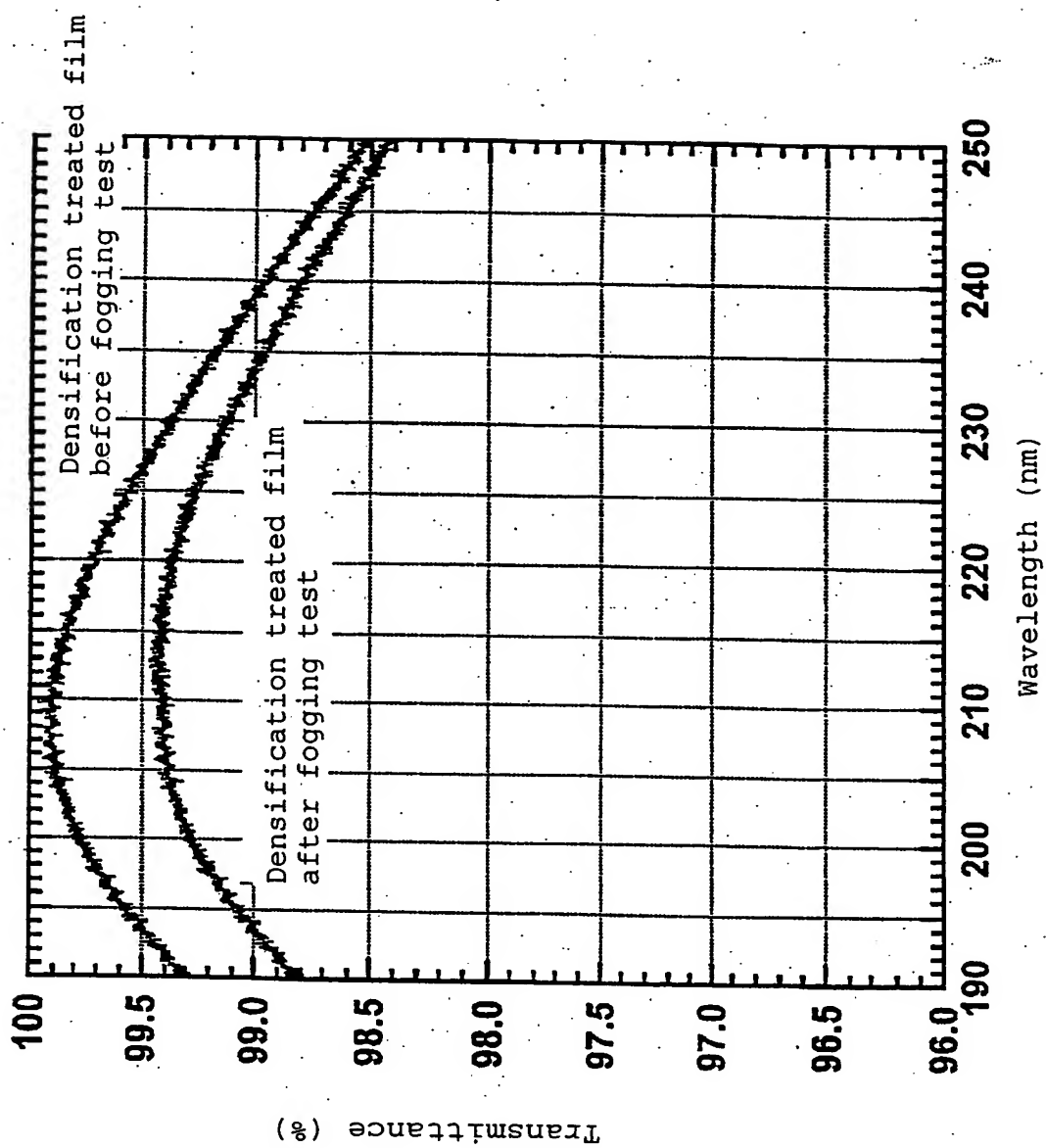
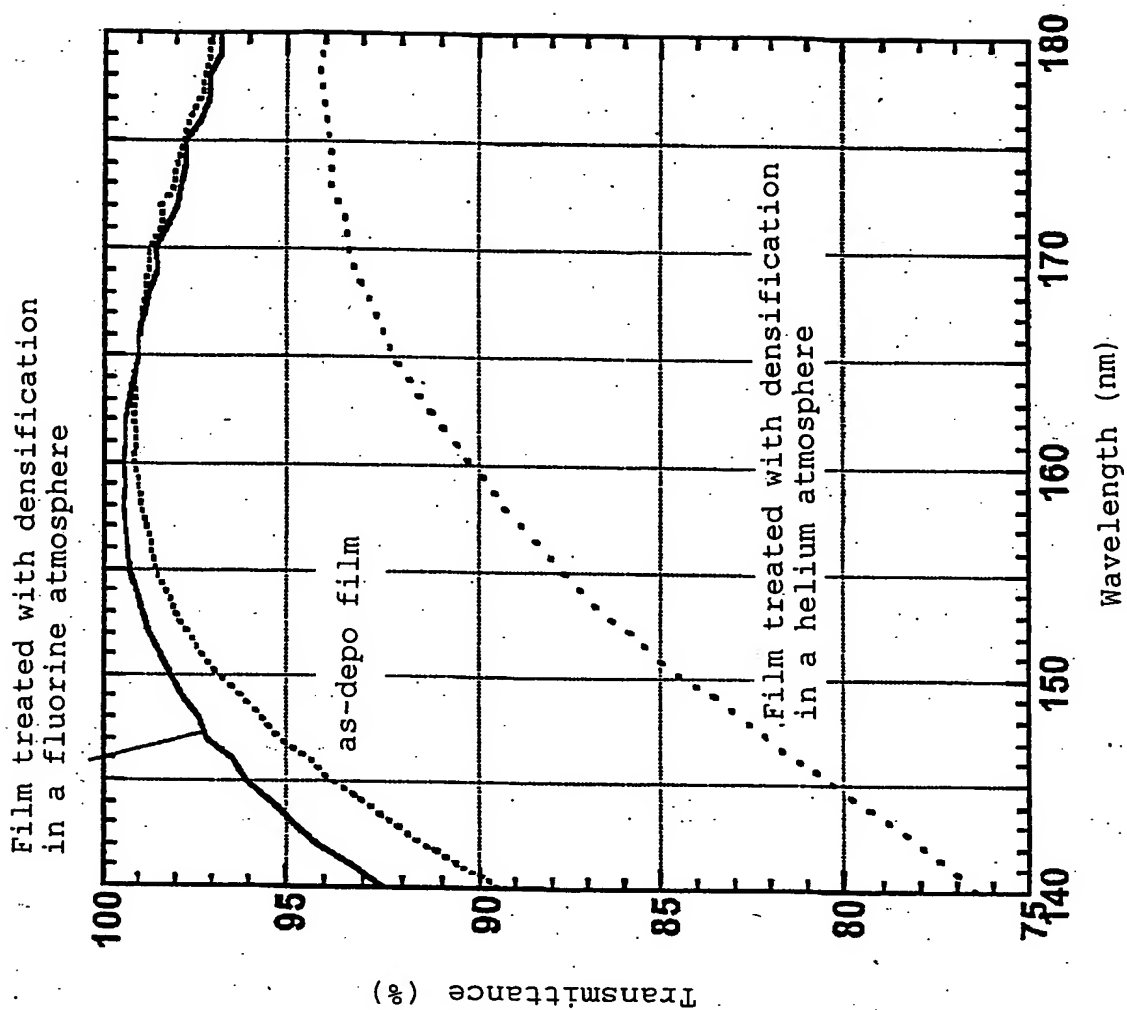


FIG. 6



DECLARATION

I, Yayoi HONDA, c/o S.SUZUKI & ASSOCIATES, 13-6,
Nishigotanda 7-chome, Shinagawa-ku, Tokyo, Japan, do solemnly
and sincerely declare that I understand the Japanese language
and the English language well, and that the attached English
version is a full, true and faithful translation made by me
of the US Provisional Application No. 60/470,900 (May 16, 2003).

I make this solemn declaration conscientiously believing
the same to be true.

November 7, 2003

A handwritten signature in cursive script, reading "Yayoi Honda".

Yayoi HONDA

[Name of Document] Specification

[Title of the Invention]

A PROCESS FOR PRODUCING FLUORIDE OPTICAL ELEMENT AND
FLUORIDE OPTICAL ELEMENT

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a process for producing a fluoride optical element and a fluoride optical element obtainable from the process. Particularly, the present invention relates to a process for producing a fluoride optical element having a smooth and cleaned surface by cleaning with polishing the surface and the contact with a fluorine type gas and a fluoride optical element having excellent surface properties obtainable from the process.

[0002]

[Background of the Invention]

Recently, circuit patterns are further fined with high integration or high densification of semiconductor integrated circuits so that the fining of the line width in circuits has been demanded. In order to produce fine circuit patterns with photo lithography, exposure with light having a shorter wavelength is required so that the development of a reduced projection exposure apparatus for producing semiconductor circuits in which vacuum ultraviolet light is used as an

exposure light source has been proceeded.

[0003]

Fluoride solids have excellent optical properties such that they are transparent in the wide light wavelength range of from a long wavelength to a short wavelength in vacuum ultraviolet region. The fluoride solids are transparent even in vacuum ultraviolet region with a wavelength of less than 180 nm differing from nitride solids or oxide solids. Therefore, the fluoride solids are necessary and indispensable materials for optical elements including lenses or prisms in the case that light in the vacuum ultraviolet region is used, for example, a reduced projection exposure apparatus for vacuum ultraviolet light.

[0004]

The general process for processing a fluoride solid into a desired optical element shape such as lenses, prisms etc includes the step of cutting, grinding, rough polishing, precision polishing (final polishing) in this order. The finished condition of the precision polishing is determined in such a way that the surface shape of the polished surface is measured by an interferometer and the value of RMS (root mean square) showing the difference between the measured value and the designed value is determined. Generally, when the RMS value on the polished surface reaches the range from several to several tens $\lambda / 1000$ wherein the wavelength (nm) of light is

represented by λ , the completion of the precision polishing is determined. That is to say, with shortening the wavelength of light used, higher finishing precision is required for the polished surface. Then, the precise polishing satisfying such conditions for the surface is completed to prepare an optical element showing the optical properties of the desired value. The resulting optical element is washed with a neutral detergent, distilled water and isopropyl alcohol in this order and thereby polishing abrasive grains or organic substances remained on the optical element surface are removed.

[0005]

The reduced projection exposure apparatus is provided with several tens fluoride optical elements having various shape and uses between a laser light source and a wafer where a semiconductor circuit is exposed. The surfaces of the fluoride optical elements are coated with a fluoride optical thin film such as an antireflection film, reflection film etc for the purpose of decreasing light reflection. The fluoride optical element materials, the fluoride optical element surfaces and the fluoride optical thin films have more or less light absorption so that the amount of light finally reached to the wafer surface becomes small considerably. In order to improve the exposure properties and the production thereof, the development of the technique for minimizing the reduction of the amount of light has been demanded.

[0006]

According to the results of the recent active studies, processes of decreasing deficiencies causing light absorption and impurity contents have been proposed for the fluoride optical element materials and the fluoride optical thin films. For example, Patent literature 1 discloses a process for producing a high purity having calcium fluoride single crystal containing small amounts of impurities by preparing a high purity having pretreated product with pretreatment using a scavenger in the step before crystal growth. Patent literature 2 discloses a process for fluoridizing the whole of a film by placing a fluorine loss fluoride thin film formed on a substrate with deposition into an active fluorine atmosphere.

[0007]

Moreover, the advent of techniques for further decreasing the light absorption loss of the fluoride optical element itself has been desired.

Under the circumstances, the present inventors have been earnestly studied and found that with respect to fluoride optical elements used for vacuum ultraviolet light having a shorter wavelength, a conventional cleaning process has a new problem after the precise polishing (final polishing).

[0008]

On the surface of a fluoride optical element prepared after the precise polishing (final polishing), polishing

abrasive grains are remained. The conventional method of cleaning the fluoride optical element surface with a neutral detergent, distilled water and isopropyl alcohol in this order can remove the most of polishing abrasive grains or organic substances remained on the optical element surface. However, the conventional cleaning cannot remove a slight amount of polishing abrasive grains stuck to the fluoride optical element surface or a processing changed layer produced on the fluoride optical element surface as a result of chemical reaction of the fluoride optical element surface with the polishing abrasive grains. The present inventors clarified that the light absorption loss caused by the polishing abrasive grains stuck to the fluoride optical element surface or the processing changed layer greatly influences light absorption loss of the whole of the fluoride optical element, and found a process of removing the polishing abrasive grains stuck or the processing changed layer. Thus, the present invention has been accomplished. These problems are not considered at all in conventional wavelength regions that fluoride optical elements are used, i.e. in the regions of infrared light, visible light and ultraviolet light.

[0009]

Patent literature 1 is JP-A-H9-315893.

Patent literature 2 is JP-A-2001-264512.

[0010]

[Object of the Invention]

The present invention has been conducted under the circumstance, it is an object of the invention to provide a process for producing a smooth and cleaned surface having fluoride optical element having a low light absorption loss by removing a slight amount of polishing abrasion grains stuck to the fluoride optical element surface or a processing changed layer produced after polishing

It is a further object of the invention is to provide a fluoride optical element prepared by the process.

[0011]

[Summary of the Invention]

The present invention relates to the followings [1] to [9].

[1] The process for producing a fluoride optical element which process comprises the step of:

(I) preparing a fluoride optical element by polishing the surface of a fluoride solid with a polishing abrasive grain and

(II) cleaning the fluoride optical element by allowing the fluoride optical element to contact with a fluorine type gas.

[2] The process for producing a fluoride optical element as described in [1] wherein the polishing abrasive grain is at least one selected from the group consisting of silicon dioxide, silicon carbide, boron carbide, cubic boron nitride

and diamond.

[3] The process for producing a fluoride optical element as described in [2] wherein the polishing abrasive grain is silicon dioxide.

[4] The process for producing a fluoride optical element as described in any one of [1] to [3] wherein the fluoride solid comprises at least one fluoride selected from the group consisting of magnesium fluoride, calcium fluoride, lithium fluoride, lanthanum fluoride, aluminum fluoride, neodymium fluoride, gadolinium fluoride, yttrium fluoride, dysprosium fluoride, barium fluoride, sodium fluoride, bismuth fluoride, strontium fluoride, lead fluoride, selenium fluoride, cryolite and chiolite.

[5] The process for producing a fluoride optical element as described in any one of [1] to [4] wherein the fluorine type gas includes a fluorine gas.

[6] The process for producing a fluoride optical element as described in any one of [1] to [4] wherein the fluorine type gas comprises a gas generated by dissociation of a fluorine containing compound of at least one selected from the group consisting of a fluorine gas, carbon fluoride, sulfur fluoride, nitrogen fluoride, metal fluoride, hydrogen fluoride, halogen fluoride and rare gas fluoride, with heat, electricity or plasma.

[7] The process for producing a fluoride optical

element as described in any one of [1] to [6] wherein in the step (II), the fluoride optical element is allowed to contact with the fluorine type gas at a temperature of from 10 to 500°C.

[8] The fluoride optical element obtainable by a process for producing a fluoride optical element as described in any one of [1] to [7].

[9] The fluoride optical element as described in [8] wherein the fluoride optical element has a difference of light absorption loss on the surfaces at 157 nm between the steps (I) and (II) of not less than 0.1 %.

[0012]

[Detailed Description of the Invention]

Hereinafter, the present invention will be described in detail.

The process for producing a fluoride optical element according to the present invention comprises the step of:

(I) preparing a fluoride optical element by polishing the surface of a fluoride solid with a polishing abrasive grain (hereinafter referred to the step (I)) and

(II) cleaning the fluoride optical element by allowing the fluoride optical element to contact with a fluorine type gas (hereinafter referred to (II)).

[0013]

As the fluoride solid of the present invention, any fluorides capable of forming fluoride optical elements are

preferably used. Specifically, it is preferred to use at least one fluoride selected from the group consisting of magnesium fluoride, calcium fluoride, lithium fluoride, lanthanum fluoride, aluminum fluoride, neodymium fluoride, gadolinium fluoride, yttrium fluoride, dysprosium fluoride, barium fluoride, sodium fluoride, bismuth fluoride, strontium fluoride, lead fluoride, selenium fluoride, cryolite and chiolite.

[0014]

The fluoride solid submitted to the step (I) is generally an almost processed solid having the desired optical element shape prepared by cutting a raw material fluoride, grinding and roughly polishing. The polishing in the step (I) corresponds to precision polishing (final polishing). In the step (I), surface polishing of the fluoride solid is conducted using a suspension prepared by dispersing polishing abrasive grains in a solvent such as water, etc.

[0015]

Generally, as polishing abrasive grain materials used in the precision polishing of the fluoride solid surface, oxides such as silicon dioxide, aluminum oxide, chromium oxide, zirconium oxide, cerium oxide etc, carbides such as silicon carbide, boron carbide etc, cubic boron nitride and diamond are known.

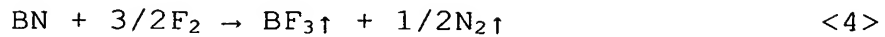
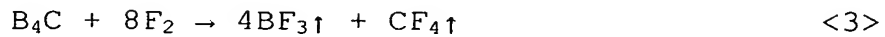
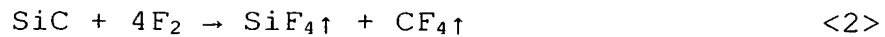
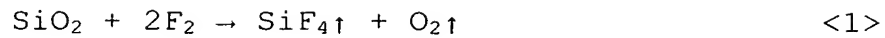
As the abrasive grain for use in the step (I) of the invention, any abrasive grain materials capable of forming a highly volatile compound by reaction with a fluorine gas can be used. The examples follow. At least one material selected from the group consisting of silicon dioxide (SiO_2), silicon carbide (SiC), boron carbide (B_4C), cubic boron nitride (BN) and diamond (C) is preferred, and particularly, silicon dioxide having excellent physical property values such as hardness is preferred as the abrasive grain for the precision polishing (final polishing) of the fluoride optical element material.

[0016]

After the fluoride optical element obtained in the step (I) is cleaned by a conventional cleaning method, on the surface of the fluoride optical element, abrasive grains stuck to the surface or a processing changed layer formed by the chemical reaction are present.

It is very difficult to remove the abrasive grains stuck to the surface or the processing changed layer formed on the surface with a physical method and to prepare a fluoride optical element having a clean surface. However, if the fluorination reaction sufficiently proceeds in the step (II) that follows the step (I), a highly volatile substance is generated by the reaction with the fluorine type gas and thereby etching removal can be performed chemically as shown in one example of the following reaction formulas <1> to <5>.

[0017]



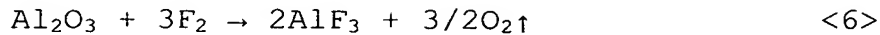
It is undesirable to use abrasive grains of materials capable of forming a low volatile compound by the reaction with the fluorine type gas, such as aluminum oxide, zirconium oxide or cerium oxide, because the remained abrasive grains are not sufficiently removed in the step (II).

[0018]

For example, on the surface of a fluoride optical element obtained by conducting the step (I) with aluminum oxide (alumina (Al_2O_3)) as abrasive grains and then conducting conventional cleaning, aluminum oxide abrasive grains stick or a processing changed layer is formed by the chemical reaction of aluminum oxide with a fluoride. On the other hand, even if the fluorination reaction sufficiently proceeds by conducting the subsequent step (II), it is difficult to remove aluminum that is as a residual element. As shown in the reaction formula (6), aluminum fluoride, which is a reaction product of the abrasive grains stuck to the fluoride optical element surface or a reaction product of the processing changed layer with the

fluorine type gas, has low volatility so that the aluminum cannot be removed from the fluoride optical element surface.

[0019]



If the polishing abrasive grains of aluminum oxide are selected as described above, aluminum fluoride remains on the fluoride optical element surface as a reaction product. It can be thought that the aluminum fluoride remained on the fluoride optical element surface is present in the state of firmly adhering or sticking to the fluoride optical element surface and in the state of a processing changed layer formed by the chemical reaction with the fluoride optical element surface. Since the aluminum fluoride itself is transparent in the vacuum ultraviolet region, it is presumed that the light absorption loss of the fluoride optical element surface is decreased by the step (II), but actually, aluminum fluoride is a chemically unstable substance, so that it is changed into aluminum oxide or aluminum hydroxide which absorbs vacuum ultraviolet light by the reaction with oxygen or moisture in the atmosphere, and as a result, the light absorption loss is occasionally increased.

[0020]

Also when polishing abrasive grains of zirconium oxide or cerium oxide are used, it is difficult to sufficiently remove the polishing abrasive grains remained in the step (I) or the

processing changed layer in the step (II) because of low volatility of zirconium fluoride or cerium fluoride that is a reaction product with a fluorine type gas, similarly to the case of using aluminum oxide. On this account, it is undesirable to select, as polishing abrasive grain, materials that form a low volatile compound by the reaction with a fluorine type gas.

[0021]

In the step (II), the cleaning of removing components derived from polishing abrasion grains from the fluoride optical element surface is carried out in such a way that the fluoride optical element having the surface polished in the step (I) is brought into contact with a fluorine type gas and thereby the components derived from a slight amount of the polishing abrasion grains remained on the fluoride optical element surface is reacted with the fluorine type gas to produce a highly volatile fluoride.

[0022]

The fluorine type gas used in the step (II) is a gas containing fluorine (F) and preferably a gas containing a fluorine gas (F_2). Further, a highly reactive fluorine gas atmosphere, e.g., a gas containing active fluorine such as fluorine radical or fluorine ion, can be selected. Preferable examples of the fluorine type gas may include a fluorine gas; carbon fluoride, such as carbon tetrafluoride; sulfur fluoride, such as sulfur hexafluoride; nitrogen fluoride, such as

nitrogen trifluoride; metal fluoride, such as manganese tetrafluoride or silver difluoride; hydrogen fluoride; halogen fluoride, such as chlorine trifluoride; or a gas atmosphere containing fluorine generated by dissociating a fluorine-containing compound containing at least one of fluorides of rare gases, such as xenon difluoride, by means of any one of heat, electricity and plasma. Additionally, the fluorine type gas may be diluted with a gas which does not react with the component derived from the polishing abrasive grains, such as rare gas and may be submitted to use.

[0023]

In the step (II), the temperature for contacting the fluoride optical element with the fluorine type gas is in the range of 10 to 500°C, preferably 50 to 400°C.

In the step (II), the elements derived from the polishing abrasive grains remained on the surface of the fluoride optical element react with the fluorine type gas, and the elements are removed as volatile substrates from the surface of the fluoride optical element. By this removal, the polishing abrasive grains stuck to the surface and the processing changed layer, which cannot be removed with physical cleaning, are favorably removed from the fluoride optical element surface and then the light absorption loss caused by the polishing abrasive grains or the processing changed layer is markedly decreased, and a

fluoride optical element having more excellent optical properties can be obtained.

[0024]

The fluoride optical element thus obtained has a small light absorption loss on the optical element surface attributable to the polishing abrasive grains or the processing changed layer, and exhibits high transmission particularly to light having a short wavelength. By the fluorination reaction, the light absorption loss of the fluoride optical element surface at 157 nm is decreased by usually not less than 0.1%, and the optical element exhibits excellent optical properties.

One example of the step (II) is described below with reference to Fig. 1, though the invention is in no way limited to the example.

[0025]

Fig. 1 shows an example of a cleaning apparatus capable of performing the step (II) of cleaning the fluoride optical element surface by contact with a fluorine type gas. In Fig. 1, numeral 1 designates a fluorine gas generation source made of nickel; numeral 2 designates a helium gas cylinder for diluting a fluorine gas; numeral 3 designates a Monel-made gas feeding tube for feeding a fluorine gas, a helium gas and a fluorine/helium mixed gas; numeral 4 designates a valve whose gas contact portion is coated with nickel; numeral 5 designates a cleaning vessel made of nickel; numeral 6 designates a nickel

made fixing jig for a fluoride optical element; numeral 7 designates a fluoride optical element; numeral 8 designates a temperature-measuring thermocouple; numeral 9 designates a PID-controllable external heater; numeral 10 designates a pressure gauge; numeral 11 designates a flow rate/pressure control means; numeral 12 designates a vent system; numeral 13 designates a fluorine gas exhaust means.

[0026]

It is desirable that the inner wall of the cleaning vessel and the jig for fixing a fluoride optical element are fluorinated by introducing a fluorine gas and heating to deposit nickel fluoride on the surfaces and thereby is subjected to passivation.

The materials of the inner wall of the cleaning vessel, the inner wall of the gas feeding tube and the gas contact portion of the valve are preferably at least one of nickel, a nickel alloy, copper, a copper alloy, aluminum and an aluminum alloy and have a chromium concentration or a titanium concentration of not more than 1%, preferably not more than 1000 ppm, more preferably not more than 100 ppm.

[0027]

After polishing the fluoride optical element, the fluorine cleaning is carried out by continuous four steps including placing the fluoride optical element, removing moisture in cleaning vessel with deaeration, fluorination

reaction and withdrawing the fluoride optical element. The step of removing moisture in the cleaning vessel with deaeration may be omitted, but the step of placing the fluoride optical element, the fluorination reaction step and the step of withdrawing the fluoride optical element are essential steps. These steps are described below in detail.

[0028]

In the step of placing the fluoride optical element, the fluoride optical element 7 subjected to conventional cleaning after precision polishing (final polishing) with a suspension prepared by dispersing polishing abrasive grains of at least one material selected from the group consisting of silicon dioxide, silicon carbide, boron carbide, cubic boron nitride and diamond in a suspension, is fixed to the jig 6 for fixing the fluoride optical element in the cleaning vessel 5, and then the cleaning vessel 5 is closed.

[0029]

In the step of removing moisture with deaeration in the cleaning vessel, the cleaning vessel 5 is evacuated to 10^{-5} Pa by means of the vent system 12, and then while introducing a helium gas into the cleaning vessel 5 through the gas pipe 3, the gas atmosphere in the cleaning vessel 5 is heated to 150°C using the external heater 9, and the cleaning vessel 5 is held in this state for 12 hours to remove moisture. For the temperature measurement, the thermocouple 8 is used. The

moisture-removing step with deaeration is effective for preventing corrosion deterioration of the inner wall of the cleaning vessel 5. Since the cleaning effect on the polished surface of the fluoride optical element is not lowered even if the moisture-removing step with deaeration is not conducted, it is possible to omit the moisture-removing step.

[0030]

In the fluorination reaction step of allowing the surface-polished fluoride optical element 7 to contact with a fluorine type gas, the fluorine gas fed from the fluorine gas generation source 1 is diluted with helium gas to have a concentration of about 1% and introduced into the cleaning vessel 5 through the gas feeding tube 3 and the valve 4. The temperature of the gas atmosphere in the cleaning vessel 5 is set at 100°C and then the fluorination reaction on the polished surface of the fluoride optical element is promoted. Using the flow rate and pressure controller 11 provided on the downstream side of the cleaning vessel 5, the pressure gauge 10 is regulated to 0.1 MPa (atmospheric pressure), and the timing is started. In this step, an open cleaning vessel in which the gas flow is continued in the opened exhaust system may be used or a closed cleaning vessel in which the gas flow is stopped in the closed exhaust system may be used. This state was continued for the prescribed period of time. In the fluorination reaction step, the conditions may be determined so as to proceed fluorination

reaction on the polished surface of the fluoride optical element, and the temperature of the gas atmosphere in the cleaning vessel 5, i.e., temperature for allowing the fluoride optical element to contact with the fluorine type gas, is determined to be from 10 to 500°C, preferably 50 to 400°C, more preferably 100 to 300°C. If the temperature is lower than 10°C, the rate of fluorination reaction is slow and the cleaning efficiency is lowered. If the temperature exceeds 500°C, a problem that the materials of the inner wall of the cleaning vessel 5 or the jig 6 for fixing the fluoride optical element is corroded and deteriorated may occur. The fluorine gas concentration may be arbitrarily selected from 1 ppm to 100%. The gas pressure may be also arbitrarily selected from 10^{-5} to 10^{-7} Pa. The term "prescribed time" used herein means a time necessary for sufficiently cleaning the polished surface of the fluoride optical element, and the time is determined according to the materials of the fluoride optical element, the material of the polishing abrasive grain or the abrasion conditions in the precision polishing (final polishing) step, and the temperature of the gas atmosphere, fluorine gas concentration and gas pressure in the cleaning vessel 5 in the fluorination reaction step. From the results of the experiments, it has been confirmed that, in the case of cleaning after polishing the surface of fluorite (calcium fluoride) with silicon dioxide (SiO_2) type polishing abrasive grains, if the temperature of the gas atmosphere in

the cleaning vessel 5 is 100°C and the fluorine concentration therein is 1%, the adequate time is 1 hour. After a lapse of the prescribed period of time, heating is stopped if the cleaning vessel 5 is heated, and then the cleaning vessel 5 is cooled until the temperature of the fluoride optical element 7 becomes about room temperature.

[0031]

In the fluorination reaction step, it is preferred to select a fluorine gas atmosphere having high reactivity, and further, it is possible to select a gas atmosphere containing fluorine generated by dissociating, with any one of heat, electricity and plasma, a fluorine compound containing at least one selected from the group consisting of fluorine gas, carbon fluoride, such as carbon tetrafluoride; sulfur fluoride, such as sulfur hexafluoride; nitrogen fluoride, such as nitrogen trifluoride; metal fluoride, such as manganese tetrafluoride or silver difluoride; hydrogen fluoride; halogen fluoride, such as chlorine trifluoride; or a fluoride containing of rare gases, such as xenon difluoride.

[0032]

In the step of taking out the fluoride optical element, introduction of the fluorine type gas is stopped, and then the cleaning vessel 5 is evacuated and thoroughly purged with helium gas. Thereafter, purging with the helium gas is stopped, and

the cleaning vessel 5 is released and the fluoride optical element completely cleaned is taken out.

In the fluorination reaction step, the polishing abrasive grains stuck to the fluoride optical element surface and the processing changed layer are removed by the fluorination reaction and thereby the fluoride optical element surface is cleaned. The surface of the fluoride optical element obtained after the cleaning in the invention becomes a fluoride having the same stoichiometric composition as that of the inside.

[0033]

The fluoride optical element of the present invention is obtainable by the process of producing the fluoride optical element as described above. Elements derived from the polishing abrasive grains are removed as volatile substances from the surface of the fluoride optical element so that the fluoride optical element has almost zero or a slight amount of a light absorption loss caused by residue of the polishing abrasive grains, high transmission toward light having a short wavelength, and usually has a surface light absorption loss at 157 nm 0.1 % or more decreased by the fluorination reaction and further excellent optical properties.

[0034]

The light absorption loss of the surface at 157 nm that is decreased by the fluorination reaction can be calculated in

the following manner from the results of vacuum ultraviolet spectrometry measurement.

The light absorption loss $L_{157\text{nm}}\%$ of the optical element at 157 nm is represented by the formula (A).

$$L_{157\text{nm}} = (\text{surface absorption loss at 157 nm}) \times 2 \\ + (\text{inside absorption loss at 157 nm}) \quad (\text{A})$$

The surface absorption loss occurs on two surfaces of the light incident surface and the light outgoing surface.

[0035]

On the other hand, the transmittance ($T_{157\text{nm}}, \%$) and the reflectance ($R_{157\text{nm}}, \%$) of the optical element at 157 nm can be measured by a vacuum ultraviolet spectrometer. The light absorption loss $L_{157\text{nm}}(\text{I})\%$ of the optical element at 157 nm after the step (I) and the light absorption loss $L_{157\text{nm}}(\text{II})\%$ thereof after the step (II) are determined by the formulas (B) and (C), respectively.

[0036]

$$L_{157\text{nm}}(\text{I}) = 100 - T_{157\text{nm}}(\text{I}) - R_{157\text{nm}}(\text{I}) \quad (\text{B})$$

$$L_{157\text{nm}}(\text{II}) = 100 - T_{157\text{nm}}(\text{II}) - R_{157\text{nm}}(\text{II}) \quad (\text{C})$$

In the formulas, $T_{157\text{nm}}(\text{I})$ and $R_{157\text{nm}}(\text{I})$ represent a transmittance and a reflectance, respectively, of the optical element at 157 nm after the step (I), and $T_{157\text{nm}}(\text{II})$ and $R_{157\text{nm}}(\text{II})$ represent a transmittance and a reflectance, respectively, of the optical element at 157 nm after the step (II).

[0037]

It is thought that the inside absorption loss at 157 nm is not changed by the fluorination reaction of the invention. Accordingly, the light absorption loss $\Delta L_{157\text{nm}}\%$ of the surface at 157 nm that is decreased by the fluorination reaction is calculated from the formula (D).

$$\Delta L_{157\text{nm}} = [L_{157\text{nm}}(\text{I}) - L_{157\text{nm}}(\text{II})]/2 \quad (\text{D})$$

[0038]

[Example]

The present invention is described in more detail with reference to the following non-limiting examples.

[0039]

Example 1

Single crystal fluorite of calcium fluoride (CaF_2) was processed to be in a parallel flat shape. The surface precise polishing (final polishing) of the single crystal fluorite was carried out by buff polishing with suede cloth dusted with a suspension prepared by dispersing silicon dioxide (SiO_2) polishing abrasive grain in water to prepare a fluorite optical element having a polished surface. The resulting fluorite optical element was successively washed with a neutral detergent, distilled water and isopropyl alcohol in a conventional method and thereby polishing abrasive grain and organic substances remained on the surface of the fluorite optical element were removed.

[0040]

Subsequently, using a washing apparatus as shown in Fig. 1, the fluorite optical element was fixed to a fluoride optical element-fixing jig 6 made of pure nickel provided in a cleaning vessel 5 made of pure nickel and thereafter the cleaning vessel 5 was sealed to store the fluorite optical element.

Next, the inside of the cleaning vessel 5 was evacuated to 10^{-5} Pa with an exhaust system 12, and then while passing helium gas through a monel metal fluorine gas feeding tube 3 into the cleaning vessel 5, the temperature of a gas atmosphere in the cleaning vessel 5 was elevated to 150°C with an external heater 9 capable of PID control, was kept for 12 hr and was deaerated to remove moisture in the cleaning vessel 5.

[0041]

Next, fluorine gas fed from a fluorine gas generator 1 was diluted with helium gas to have a concentration of 1% and introduced into the cleaning vessel 5 through the gas feeding tube 3 and a valve 4 which gas-contacting portions were treated with nickel coating. In the fluorine gas generator 1, a nickel vessel filled with a fluoronickel compound was used. Using the external heater 9, the fluorine gas generator 1 was heated at 350°C, and dissociation was caused by thermal decomposition of the fluoronickel compound to generate fluorine gas. The temperature of the gas atmosphere in the cleaning vessel 5 was set to 100°C. Using a flow rate/pressure controller 11 disposed in the downstream side of the cleaning vessel 5, the indicated

value of a pressure gauge 10 was regulated to be 0.1 MPa (atmospheric pressure) and timing was started. An exhaust system 12 was released and gas passing was continued for 1 hr and thereby fluorination reaction on the polished surface of the fluorite optical element surface was advanced. After the passage of 1 hr, the temperature of the cleaning vessel 5 was cooled to room temperature, and thereby the fluorination reaction was finished.

[0042]

Next, fluorine gas introduction was stopped and the cleaning vessel 5 was evacuated followed by sufficiently purging with helium gas. Thereafter, the purging with helium gas was stopped and the cleaning vessel was released, and the fluorite optical element 1 treated with cleaning treatment completely was taken out.

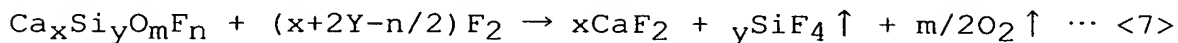
The polished surface of the resulting fluorite optical element 1 was measured by TOF-SIMS (time of flight secondary ion mass spectrometer) and the results are shown in Table 2. From Fig. 2, it was confirmed that the fluorite optical element 1 prepared in Example 1 had higher detected amounts of both elements of Ca atom and F element as compared with the surface of a fluorite optical element 2 prepared in Comparative Example 1 as described later, and had a F/Ca ratio of 2 which was an almost stoichiometric composition. Further, Si atom was not detected at all, and O atom was detected slightly. It is

considered that the O atom slightly detected originated from physical absorbed water.

[0043]

This result showed that in Example 1, SiO₂ used as a polishing abrasive gain was stuck on the surface of the fluorite optical element and/or chemical reaction between SiO₂ and CaF₂ on the fluorite optical element surface produced a processing changed layer (Ca_xSi_yO_mF_n), and the gain and/or the processing changed layer were reacted with fluorine gas as shown in the formula <1> or the following formula <7> and they were chemically removed with etching and thereby cleaned.

[0044]



The transmittance spectrum T (%) and the reflectance spectrum R (%) of the resultant fluorite optical element 1 were measured with a vacuum ultraviolet spectroscopy and a light absorption loss (100-T-R (%)) was determined. The transmittance spectrum T(%) is shown in Fig. 3 and the light absorption loss (100-T-R (%)) is shown in Fig. 4.

[0045]

Figs. 3 and 4 showed that the fluorite optical element 1 prepared in Example 1 had a lower absorbing loss and a higher transmittance in the region of a wavelength of less than 160 nm as compared with a fluorite optical element 2 subjected to conventional polishing and cleaning prepared in Comparative

Example 1, as described later. Further, it was found that the difference between the element of Example 1 and the element of Comparative example 1 became more clearly with shortening the wavelength.

As is clear from the above, it was confirmed that by the production process of the fluoride optical element according to the present invention, it was possible to remove easily the processing changed layer derived from silicon dioxide (SiO_2) polishing abrasive gains which was not removed by conventional polishing and cleaning methods, and almost complete fluoride optical element having a smooth surface and a low absorption loss on the polished surface could be formed.

[0046]

Still, the fluorite optical element 1 prepared in Example 1 was confirmed to have an absorption loss of about 1% in a short wavelength region, and it was considered that this was caused due to absorption of the fluorite inside.

As is also clear from the above, the polishing and cleaning of the production process of the fluoride products according to the present invention are extremely effective in optical uses for the next generation in a wavelength of not more than 160 nm, such as F_2 (157 nm) lithography or the like, and further, the effectiveness to polishing and cleaning by conventional methods is increased with shortening the wavelength used.

[0047]

The resultant fluorite optical element 1 and the fluorite optical element 2 prepared in Comparative Example 1 as described below were observed on the unevenness of the surfaces thereof by an inter-atomic microscope. In result, a marked difference of smoothness between them was not found so that the production process of the present invention is applicable for fluoride optical elements with no problems.

[0048]

Comparative Example 1

Fluorite processed in a parallel flat shape was subjected to buff polishing in the same manner as in Example 1, to prepare a fluorite optical element having a polished surface.

Subsequently, the resulting fluorite optical element was successively washed with a neutral detergent, distilled water and isopropyl alcohol in a conventional method and thereby polishing abrasive grains and organic substances remained in the surface of the fluorite optical element were removed, to prepare a fluorite optical element 2.

[0049]

The polished surface of the resulting fluorite optical element 2 was measured with TOF-SIMS (time of flight secondary ion mass spectrometer) in the same manner as in Example 1. The results are shown in Fig. 2 together with the results of Example 1. In the fluorite optical element 2, the F/Ca ratio was considerably lower as compared with the stoichiometric

composition of 2 and very large amounts of Si atom and O atom were detected in addition to Ca atom and F atom. From this fact, it is considered that the fluorite optical element 2 was in a state that silicon dioxide (SiO_2) used as polishing abrasive gains was stuck on the surface of the fluorite optical element and/or chemical reaction between SiO_2 and CaF_2 on the fluorite optical element surface produced a processing changed layer ($\text{Ca}_x\text{Si}_y\text{O}_m\text{F}_n$). From this result, it is clear that conventional polishing and cleaning methods cannot remove polishing abrasive gains (Si atom or O atom) remained on the fluorite optical element surface after polishing.

[0050]

The transmittance spectrum T (%) and the reflectance spectrum R (%) of the resultant fluorite optical element 2 were measured with a vacuum ultraviolet spectroscopy in the same manner as in Example 1 and light absorption loss ($100-T-R$ (%)) was determined. The transmittance spectrum T (%) is shown in Fig. 3 and the light absorption loss ($100-T-R$ (%)) is shown in Fig. 4 together with the results of Example 1.

It was found that when the wavelength is not more than 160 nm, the transmittance lowers because light absorption generates due to the polishing abrasive gains remained on the fluorite optical element surface.

[0051]

Example 2

The procedure of Example 1 was repeated except that the fluorine gas generator 1 in the cleaning apparatus as shown in Fig. 1 was changed to an electrolytic cell of hydrogen fluoride (HF) as shown in Fig. 5 and cleaning treatment of a fluorite optical element was carried out.

In Fig. 5, the number 15 denotes an electrolytic cell, 16 denotes hydrogen gas, 17 denotes a cathode, 18 denotes a diaphragm, 19 denotes a direct current voltage source, 20 denotes an insulator, 21 is fluorine gas, 22 denotes an anode and 23 denotes a electrolyte. The electrolyte 23 was a molten mixture of hydrogen fluoride and potassium fluoride (KF) (a molar composition ratio HF/KF of 2) and electrolysis was conducted at about 100°C to generate fluorine gas.

[0052]

The fluorite optical element prepared from the treatment was analyzed by the same method as in Example 1. In result, it was confirmed that the fluorite optical element was equivalent to the fluorite optical element 1 prepared in Example 1. From the result, it was clarified that according to the production process of the fluoride optical element of the present invention, even in the case of selecting the hydrogen fluoride electrolytic cell as a fluorine gas generator, the processing changed layer derived from silicon dioxide polishing abrasive gains can be easily removed although it cannot be removed by conventional polishing and cleaning methods, and

almost complete fluoride optical element surface which is smooth and has a low absorption loss on the polished surface can be formed.

[0053]

Example 3

The procedure of Example 1 was repeated except that the fluorine gas generator 1 in the cleaning apparatus as shown in Fig. 1 was changed to a monel cylinder filled with fluorine gas and cleaning treatment of a fluorite optical element was carried out.

The fluorite optical element prepared from the treatment was analyzed by the same method as in Example 1. In result, it was confirmed that the fluorite optical element was equivalent to the fluorite optical element 1 prepared in Example 1.

[0054]

From the result, it was clarified that according to the production process of the fluoride optical elements of the present invention, even in the case of selecting the cylinder filled with fluorine gas as a fluorine gas generator, the processing changed layer derived from silicon dioxide polishing abrasive gains can be easily removed although it cannot be removed by conventional polishing and cleaning methods, and almost complete fluoride optical element surface which is smooth and has a low absorption loss on the polished surface

can be formed.

[0055]

Example 4

The procedure of Example 1 was repeated except that the fluorine gas generator 1 in the cleaning apparatus as shown in Fig. 1 was changed to a carbon tetrafluoride gas (CF_4) plasma generator as shown in Fig. 6 and the cleaning treatment conditions with the fluorination were changed, and cleaning treatment of a fluorite optical element was carried out.

[0056]

In Fig. 6, the number 24 denotes a plasma chamber, 25 denotes carbon tetrafluoride gas, 26 denotes an anode, 27 and 28 denote earth wires, 29 denotes a high-frequency electric source, 30 denotes a blocking condenser, 31 denotes an insulator, 32 denotes a cathode, 33 denotes a fluorine-containing gas and 34 denotes plasma. In this system, carbon tetrafluoride was plasma decomposed in a high frequency of 13.56 MHz, in an output of 100 W at a gas pressure in the plasma chamber of 10 Pa, to generate a fluorine (F)-containing gas. The fluorine (F)-containing gas generated from the plasma chamber was introduced into a cleaning vessel 5 through a gas feeding tube 3 and valve 4 which gas-contacting portions were treated with nickel coating. The temperature of the gas atmosphere in the cleaning vessel 5 was set at 300°C. Using a flow rate/pressure controller 11 disposed in the downstream side of the cleaning

vessel 5, the indicated value of a pressure gauge 10 was regulated to be 10 MPa (atmospheric pressure) and timing was started. An exhaust system 12 was released and gas passing was continued for 1 hr and thereby fluorination reaction on the polished surface of the fluorite optical element was advanced. After the passage of 1 hr, the temperature of the cleaning vessel 5 was cooled to room temperature, and thereby the fluorination reaction was finished.

[0057]

The fluorite optical element prepared from the treatment was analyzed by the same method as in Example 1. In result, it was confirmed that the fluorite optical element was equivalent to the fluorite optical element 1 prepared in Example 1.

From the result, it was clarified that according to the production process of the fluoride optical elements of the present invention, even in the case of selecting the carbon tetrafluoride plasma generator as a fluorine gas generator, the processing changed layer derived from silicon dioxide polishing abrasive gains can be easily removed although it cannot be removed by conventional polishing and cleaning methods, and almost complete fluoride optical element surface which is smooth and has a low absorption loss on the polished surface can be formed.

[0058]

Comparative Example 2

Fluorite processed in a parallel flat shape was subjected to buff polishing in the same manner as in Example 1, to prepare a fluorite optical element having a polished surface.

Subsequently, the resulting fluorite optical element was treated using other polishing abrasive gains such as cerium oxide or the like to remove a processing changed layer physically. Thereafter, the resulting fluorite optical element was successively washed with a neutral detergent, distilled water and isopropyl alcohol in a conventional method. However, it was confirmed that the polishing abrasive grains were remained in the surface of the fluorite optical element after the final polishing, and light absorption derived from the polishing abrasive gains was generated.

[0059]

[Effect of the Invention]

According to the present invention, polishing abrasion grains stuck to the surface of a fluoride optical element and a processing changed layer formed by reaction of the fluoride optical element surface with the polishing abrasion grains can be efficiently removed, and thereby a process for easily and efficiently producing a fluoride optical element having the surface composition almost same as the inside composition, a smooth and cleaned surface and also a very small light

absorption loss for light having a short wavelength on the surface, and a fluoride optical element can be prepared.

The fluoride optical element of the present invention has a smooth and cleaned surface and a very small light absorption loss for light having a short wavelength so that it is suitable for use as an optical element in the vacuum ultraviolet region.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a view showing one embodiment of a cleaning apparatus capable of carrying out the step (II) according to the present invention.

Fig. 2 shows the results of TOF-SIMS measurements of optical elements obtained in Example 1 and Comparative Example 1.

Fig. 3 shows vacuum ultraviolet transmittance spectra of optical elements obtained in Example 1 and Comparative Example 1.

Fig. 4 shows vacuum ultraviolet absorption loss spectra of optical elements obtained in Example 1 and Comparative Example 1.

Fig. 5 is a schematic view of a fluorine generator used in Example 2.

Fig. 6 is a schematic view of a fluorine generator used in Example 4.

- 1: fluorine gas generator
- 2: helium gas cylinder
- 3: gas feeding tube,
- 4: valve
- 5: cleaning vessel
- 6: jig for fixing fluoride optical element
- 7: fluoride optical element
- 8: temperature-measuring thermocouple
- 9: external heater
- 10: pressure gauge
- 11: flow rate/pressure controller
- 12: vent system
- 13: fluorine gas exhaust means
- 14: external heater
- 15: electrolytic cell
- 16: hydrogen gas
- 17: cathode
- 18: diagram
- 19: direct current voltage source
- 20: insulator
- 21: fluorine gas
- 22: anode
- 23: electrolyte
- 24: plasma chamber
- 25: carbon tetrafluoride gas

- 26: anode
- 27: earth wires
- 28: earth wires
- 29: high-frequency electric source
- 30: blocking condenser
- 31: insulator
- 32: cathode
- 33: fluorine (F) containing gas
- 34: plasma



FIG. 1

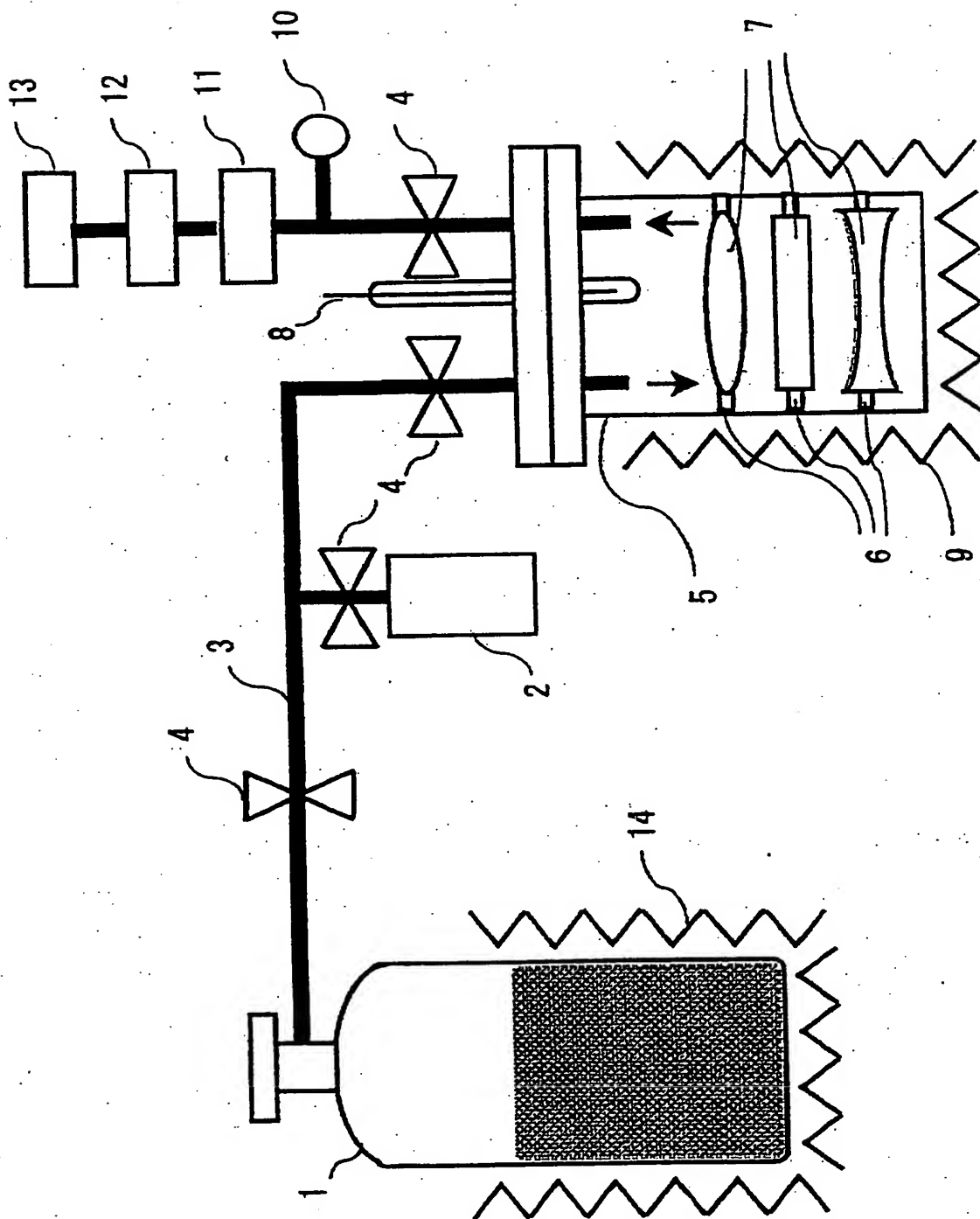




FIG. 2

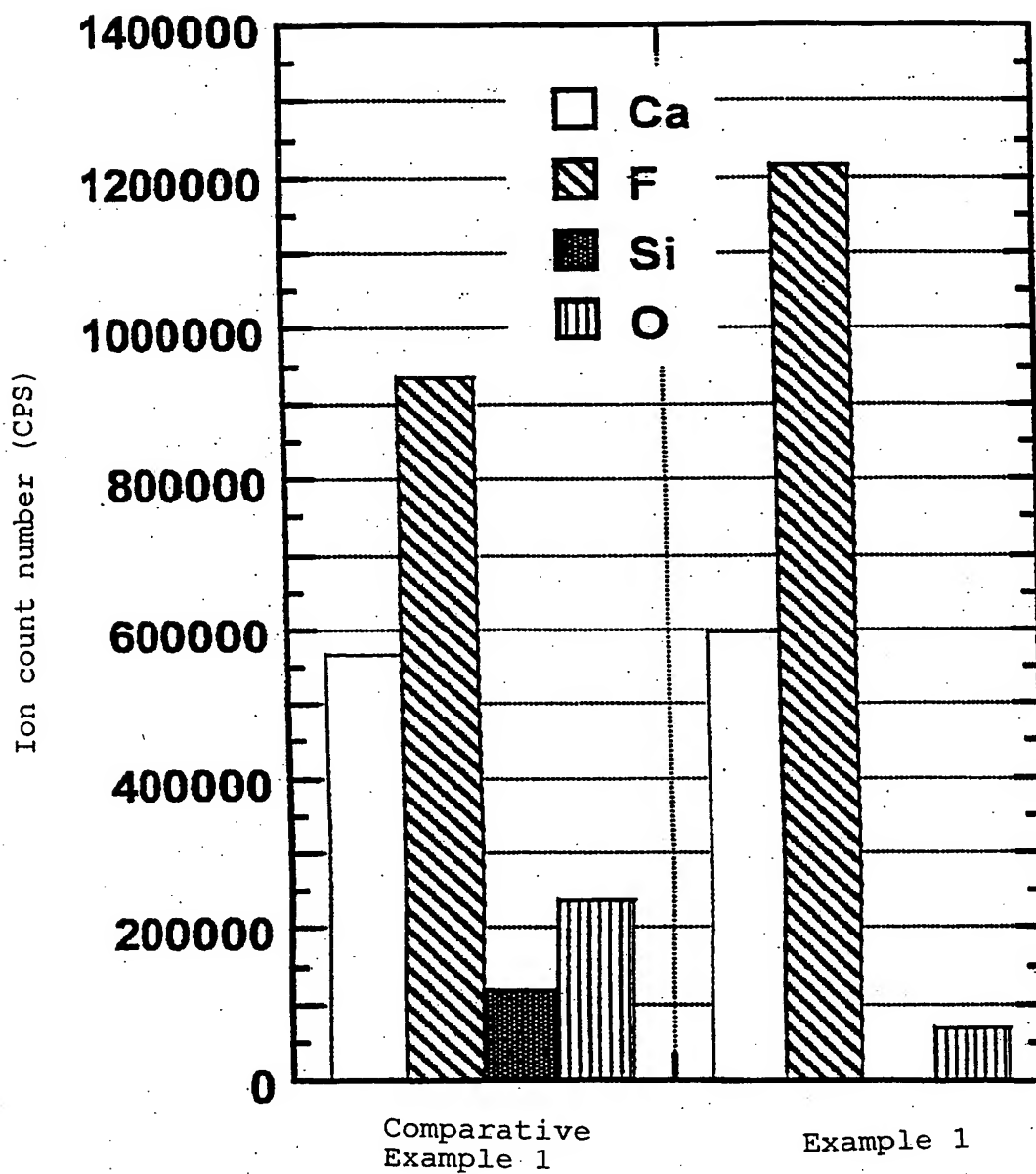


FIG. 3

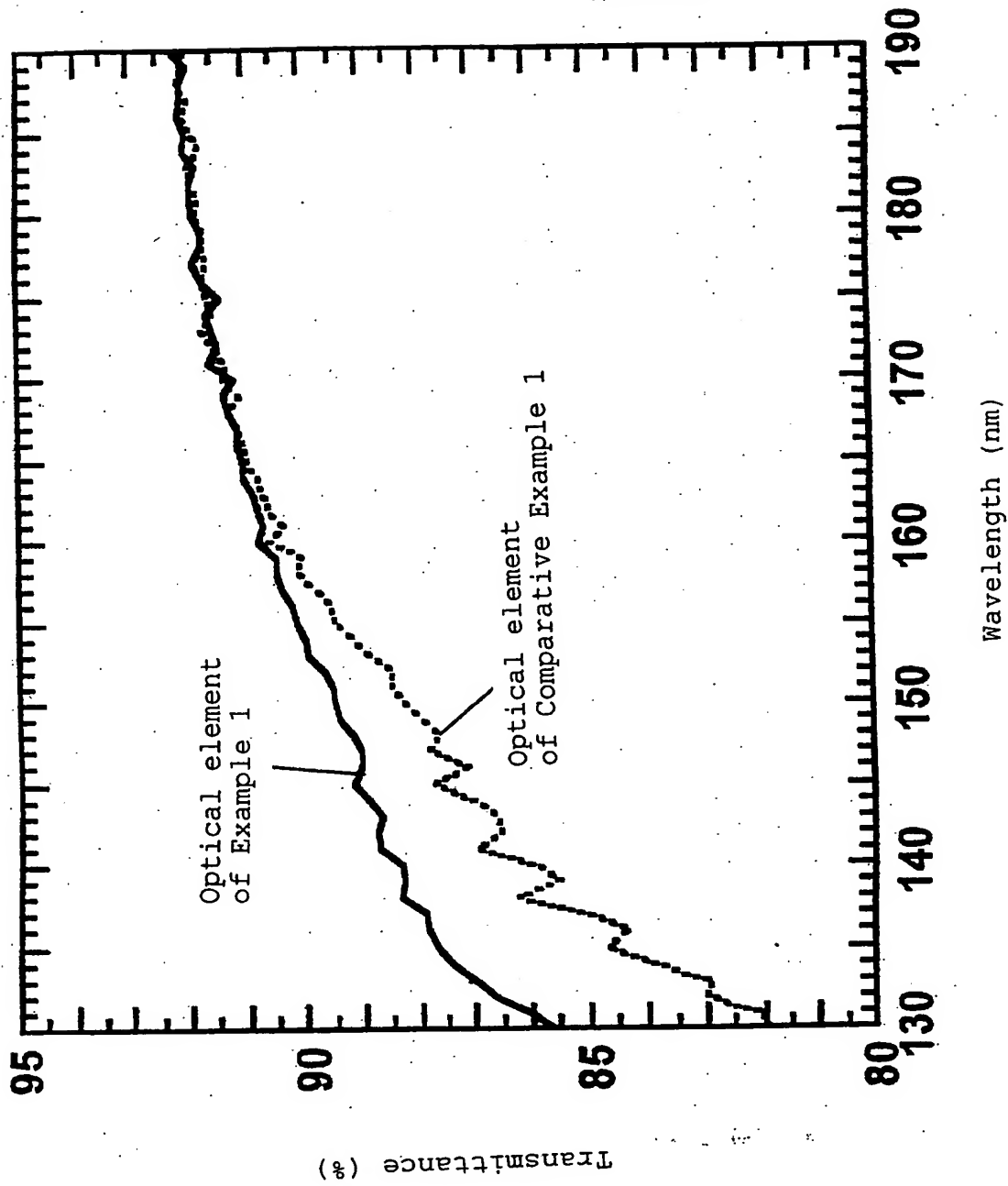


FIG. 4

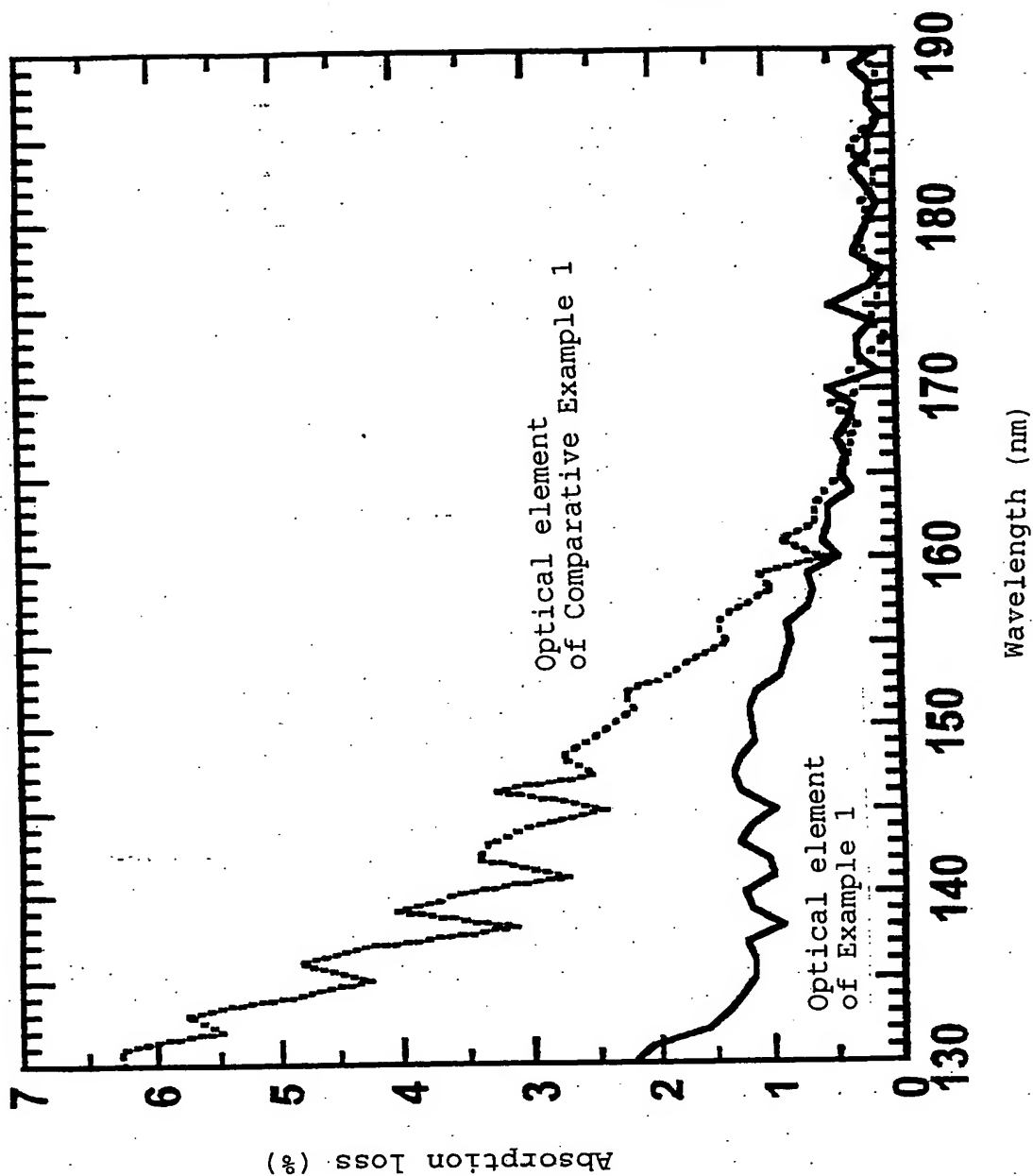


FIG. 5

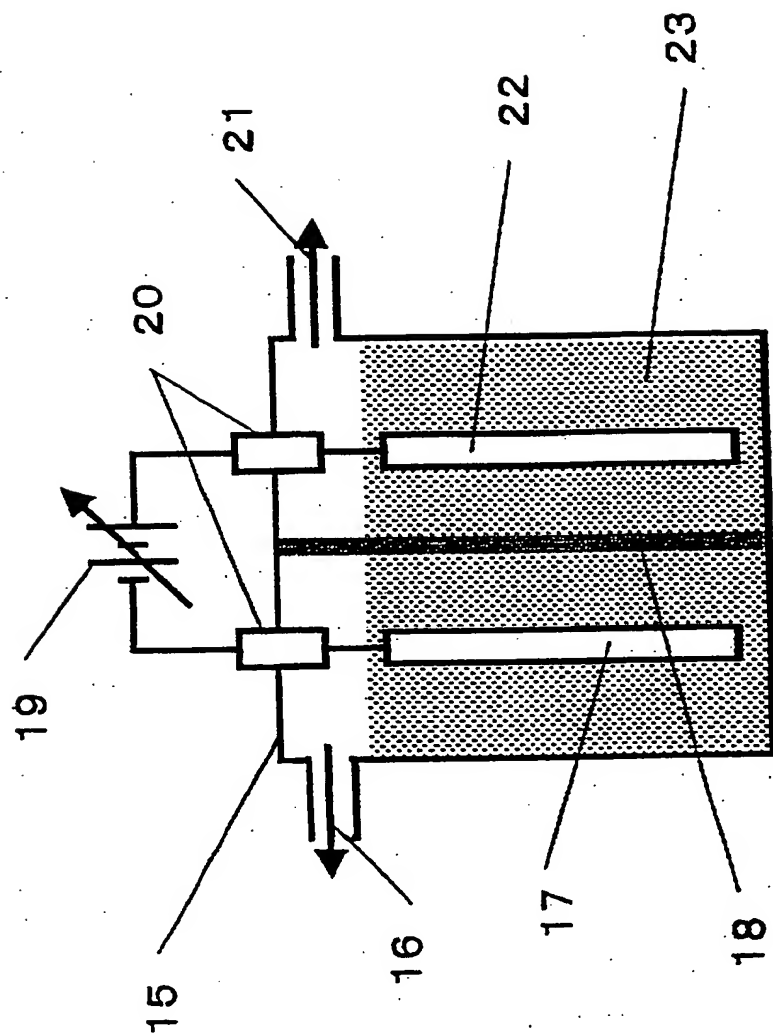


FIG. 6

